CHEMISTRY LIBRARY Sep 12 58

JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

UNIVERSITY OF MINNESOTA LIBRARIES SEP 19 1958

VOL. XXXV MAY, 1958 No. 5

CONTENTS

		PAGE
58.	Spectrophotometric studies on ferrous complexes of quinoline- and pyridine-carboxylic acids. Part I. Ferrous quinaldinate system.—By Bireswar Banerjee and Priyadaranjan Rây	297
59	Dependence of the electrokinetic potential on the dielectric constant of the medium. Part I. The glass system.—By S. N. Mukherjee and S. Chatterjee ...	304
60.	The ϕ-scale of potential and its application to some electrochemical problems. Part I. The null-points of metals and the definition of the scale of potentials.—By L. I. Antropov	309
61.	Stability and electrokinetic potential of aluminium oxide hydrosol.—By B. N. Ghosh and D. K. Chattoraj	315
62.	Estimation of formates by oxidation with mercuric chloride.—By Sameer Bose ...	320
63.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part III. Lead acetato complexes and lead propionato complexes.—By S. K. Siddhanta and S. N. Banerjee	323
64.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part IV. Cobalt mono-acetato complex.—By S. K. Siddhanta and S. N. Banerjee	339
65.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part V. Cobalt acetato complexes.—By S. K. Siddhanta and S. N. Banerjee	343
66.	Some aliphatic monocarboxylate complexes of bivalent metals in aqueous solution. Part VI. Manganese mono-acetato complex.—By S. K. Siddhanta and S. N. Banerjee	349
67.	Compounds of nickel iodide with amines and heterocyclic bases.—By Sarju Prasad and V. Krishnan	352
68.	Malate complex of copper.—By Ch. B. Nanda and S. Pani	355
69.	Synthesis of 8-aminoquinolines. Part VIII.—By A Raychaudhuri, Arun Bose and U. P. Basu	361
70.	Stereochemistry of heterocyclic compounds. Part I. Conformational analysis of ajmaline, ajmalidine, serpinine and rauwolfinine- the dihydro-indole alkaloids of Rauwolfia.—By N. Venkateswaran and Asima Chatterjee ...	363

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTCAL BALANCE

CAPACITY: 200 Gms.

SENSITIVITY: $\frac{1}{10}$ Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HERAEUS - OVENS

JULIUS PETER - BOMB CALORIMETER

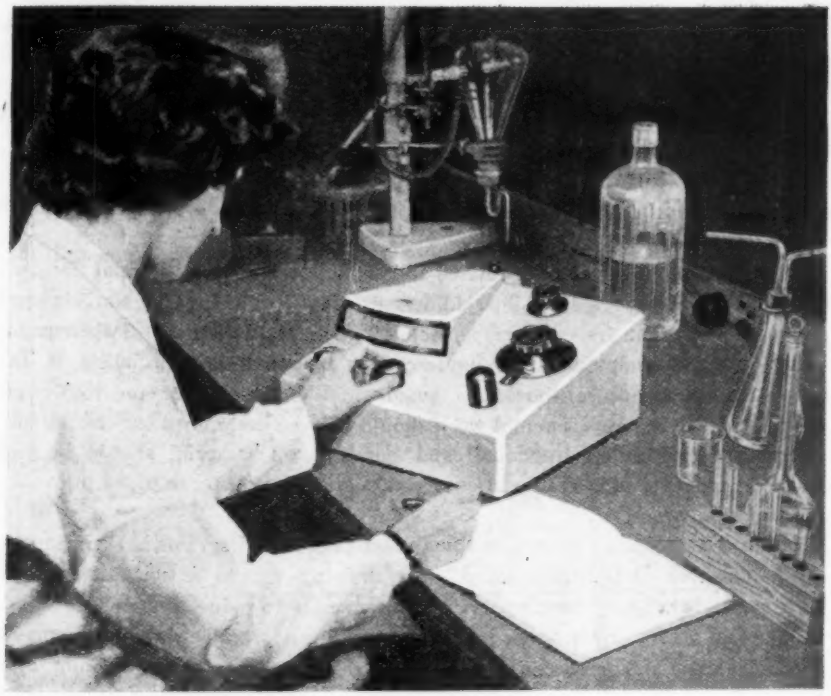
HOPPLER - VISCOMETERS

Distributors:

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

A VALUABLE INSTRUMENT FOR CHEMICAL ANALYSIS



UNICAM SP 1400 ABSORPTIOMETER

It offers rapid and accurate determination of colorimetric estimations within the visible range of the spectrum. The use of a glass prism allows the operator to select instantly any wavelength from 400—700 millimicrons with a band width that shows a marked ipmrovement on that of conventional filter type colorimeters. The wavelength setting is exactly reproducible. Reactions in which colour changes occur may be followed readily by using the continuous spectrum offered by the prism.

SOLE DISTRIBUTORS:

THE SCIENTIFIC INSTRUMENT CO. LTD.

ALLAHABAD, BOMBAY, CALCUTTA, MADRAS, NEW DELHI.

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted *in duplicate* in typescript with double line and marginal spacings. Tables and foot-notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm, c.c., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication ; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "(Found:——; ——. —— requires —— %)". Analytical results for compounds which have been previously known should be given in the form: "(Found:——; ——. Calc. for——: ——; ——%) "

12. Every paper must be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

15. **Notes will be given priority in publication.**

Change of address should be immediately intimated to the office.

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue	**Rs. 3**		
Annual Subscription	**,, 20 (for Fellows)**	**20**	**25**
,,	**,, 24 (for Subscribers)**	**28**	**32**

Inland Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page	...	Rs. 40/-
Half Page	...	,, 25/-
Quarter Page	...	,, 15/-

In Cover Pages :		**In special positions :**	
Cover (Back) Full	Rs. 100/-	Page facing first reading matter	Rs. 70/-
,, ,, Half	,, 60/-	Page facing last page of reading matter	,, 60/-
Second and Third Pages :			
Full Page	Rs. 70/-	Page facing inside front cover	,, 50/-
Half Page	,, 40/-	Page facing inside back cover	,, 50/-
Quarter Page	,, 25/-		

Closing date for advertising materials : 7th of the previous month.

10% *Rebate allowed in cases of six consecutive full and half page insertions.*

All communications are to be addressed to :

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road. Calcutta-9.

'P Y R E X'

REGD. TRADE MARK BRAND

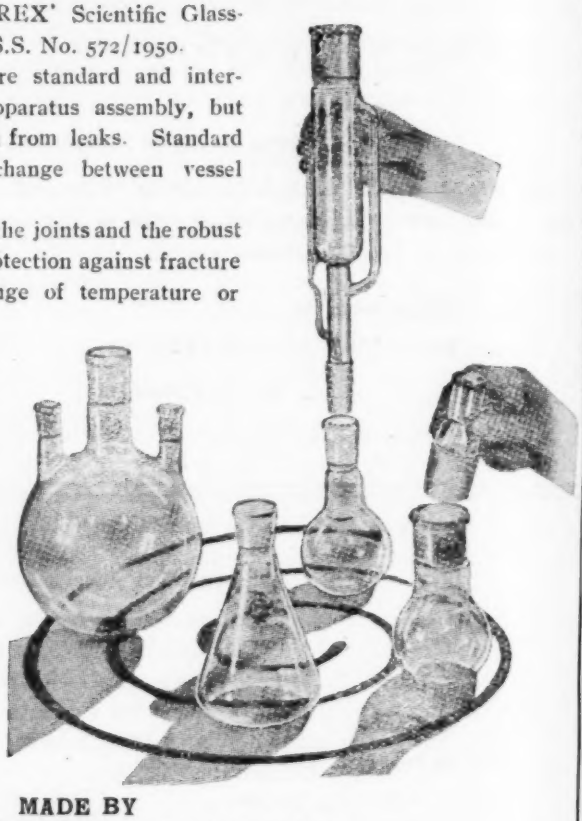
STANDARD INTERCHANGEABLE GROUND GLASS JOINTS SIMPLIFY APPARATUS ASSEMBLY

The practical development of 'PYREX' Scientific Glassware is strictly in accordance with B.S.S. No. 572/1950.

Because these ground glass joints are standard and interchangeable, they not only simplify apparatus assembly, but also ensure perfect fit and freedom from leaks. Standard adaptors make possible smooth interchange between vessel and vessel.

In addition, the sturdy strength of the joints and the robust walling of the tubing are a distinct protection against fracture whether this be due to rapid exchange of temperature or actual physical shock.

These characteristics make 'PYREX' Scientific Glassware distinctly safer and more reliable than ordinary glassware thus leading to greater economy in usage.



'PYREX'

Laboratory

and

Scientific

Glassware

MADE BY

JAMES A. JOBLING & CO. LTD.

WEAR GLASS WORKS, SUNDERLAND, ENGLAND

The original and only makers of 'PYREX' Brand glass in the United Kingdom

SOLE AGENTS IN INDIA :

GORDHANDAS DESAI PRIVATE LTD.

PHEROZESHAH MEHTA ROAD, BOMBAY-1.

Branches :

P-7 Mission Row Extension CALCUTTA 1.

4/2B, Asaf Ali Road, NEW DELHI.

22, Linghi Chetty Street, MADRAS 1.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

SPECTROPHOTOMETRIC STUDIES ON FERROUS COMPLEXES OF QUINOLINE- AND PYRIDINE CARBOXYLIC ACIDS. PART I. FERROUS QUINALDINATE SYSTEM

By Bireswar Banerjee and Privadaranjan Rây

The colour of the sparingly soluble ferrous complex with quinaldinic acid has been found to give its maximum intensity between p_H 5.8 and 7, and the wave-length for maximum absorption at 500 mμ. The intensity of the coloured solution increases in presence of an excess of KCN and to some extent with pyridine, both of which make the complex readily soluble. The colour system obeys Beer's law even in the presence of KCN, maximum absorption with the latter lying at 515 mμ.

The composition of the coloured system is given by $Fe(C_{10}H_6O_2N)_2$ with an instability constant, 3.63×10^{-6}.

Pyridine- and quinoline-carboxylic acids with a carboxyl group in the α-position to the nitrogen atom of the heterocyclic ring have long been known to exhibit intense yellow to red coloration with ferrous ion (Skraup, *Monatsh.*, 1886, **7**, 210) in not too acid or alkaline solution. Utilisation of this colour reaction for the quantitative estimation of ferrous iron with quinaldinic acid was first made by Rây and Bose (*Z. anal. Chem.*, 1933, **95**, 400) in presence of potassium cyanide, which was found to intensify the colour to a great extent. Subsequently the method was critically studied and its usefulness confirmed by Majumdar and Sen (this *Journal*, 1950, **27**, 245). Majumdar and Sen (*Anal. Chim. Acta*, 1953, **8**, 369) also employed picolinic acid for the estimation of ferrous iron and determined the composition of the coloured complex by Job's method (Job, *Compt. rend.*, 1925, **180**, 928), and found that two molecules of the ligand were bound to each ferrous ion.

Wenger *et al.* (*Helv. Chim. Acta*, 1952, **35**, 396, 569) determined the dissociation constant of quinaldinic acid and the instability constant of the coloured complex of ferrous quinaldinate, assuming the composition of the complex as given by Rây and Bose (*loc. cit.*) from an analysis of the solid compound, namely $Fe(C_{10}H_6O_2N)_2.5H_2O$. The value of this constant found is 2.6×10^{-8}.

Shimra *et al.* (*J. Chem. Soc. Japan*, 1954, **75**, **I**, 44) determined the composition of ferrous picolinate and quinaldinate in solution and came to the conclusion that both formed 1 : 3 complex in solution. As the results obtained by different workers for ferrous picolinate and quinaldinate complexes are somewhat contradictory, it has been considered worthwhile to reinvestigate the problem and to extend the study to other pyridine carboxylic acids which react with ferrous iron, affording characteristic coloured complexes.

It has now been confirmed that the composition of the ferrous quinaldinate in aqueous solution can be represented by the formula $Fe(C_{10}H_6O_2N)_2$, giving 1 : 2 complex, contrary to the finding of the Japanese workers (*loc. cit.*), but in agreement with Rây and Bose's results (*loc. cit.*) for the solid complex. The value of the instability constant 3.63×10^{-6}, as determined from the results of the present work, differs,

however, from that obtained by Wenger *et al.* (*loc. cit.*; 2.6×10^{-8}). This might be attributed to the difference in p_H values and the wave-lengths at which the measurements were made in the two cases. Wenger *et al.* (*loc. cit.*) found that the optical density of the solution remained more or less constant at or about p_H 3.6 – 4.7. They used a violet filter in a Specker-Hilger absorptiometer. In the present work it has been found that the maximum optical density of the solution lies between p_H 5.8 and 7 for 500 mμ, which differs from the values given by Wenger *et al.*

The ferrous quinaldinate complex was found in two different coloured forms, dark red and blue-violet, by Rây and Bose (*loc. cit.*), differing in their solubility. This was ascribed by them to two different configurations of the complex, *cis* and *trans*.

The occurrence of a planar 4-covalent structure of ferrous iron is rather unusual, as in most of its complexes it shows an octahedral configuration. As the solid complex, given by Rây and Bose (*loc. cit.*), contains 5 molecules of water, it might be represented better by an octahedral configuration with two of the five molecules of water being bound to the iron atom in the complex zone.

The role of potassium cyanide in intensifying the colour of the solution of the ferrous quinaldinate complex possibly lies in the formation of a cyano-complex in solution in which one or two of the water molecules are replaced by the cyanogen group. This accounts for the increased solubility of ferrous quinaldinate in potassium cyanide solution, due to the formation of an anionic complex. The intensity of the colour of the ferrous complex increases with the increasing amount of potassium cyanide and then reaches a maximum and constant value beyond which no further change occurs, but the wave-length of absorption maximum (λ_{max}) remains unchanged. This is rather unusual. On keeping these ferrous quinaldinate solutions, a colour change occurs after about 72 hours, which increases with time and then decreases again, the solution finally becoming practically free from any characteristic colour. This is particularly noticeable with comparatively small or moderate amount of potassium cyanide present. The colour changes from pink-red to brownish pink and the absorption shifts towards the ultraviolet.

The addition of pyridine has practically the same effect as that of potassium cyanide, though to a smaller extent, upon the colour intensity. There is, however, one difference that unlike potassium cyanide, it does not lead to a maximum or constant absorption value, though the colour is intensified. The intensity of the colour continues to increase with the increasing amount of pyridine added. The absorption maximum of the solution is finally shifted towards the ultraviolet. The pyridine containing solutions of the coloured quinaldinate complex, however, on keeping for 2 to 3 days, deposit a dark chocolate crystalline product. This can, in fact, be readily obtained by adding moderate amount of pyridine to a strong solution of quinaldinic acid and ferrous salt. The compound on analysis was found to possess no definite composition, but gave values corresponding approximately to the formula of a mixed pyridine-substituted complex :

$$[Fe(C_{10}H_6O_2N)_2.(C_5H_5N)_2].2[Fe(C_{10}H_6O_2N)_2.(C_5H_5N).H_2O]$$

EXPERIMENTAL

The optical density measurements in the visible region in all these experiments were made with a Unicam SP 600 spectrophotometer, using glass cells having either 1 cm or 2 cm cross-section. For p_H measurements a Cambridge Bench type p_H-meter with glass electrode and a calomel reference electrode was employed. The reagents used were all guaranteed quality reagent (Merck or B.D.H.). Reagent quality pyridine required for this work was always freshly distilled before use. All the reagents were used in aquoeus solutions.

Ferrous quinaldinate, as already stated, though sparingly soluble, still gives a solution of sufficient concentration for colorimetric measurements. The solution yields a pink-red colour even when the metal is present in traces. The optical density of the solution, measured at 500 mμ between p_H 5.8 and 7, was found to obey Beer's law for ferrous ion concentration above 5 p.p.m., and gave a sensitivity of 0.036γ ferrous ion per cm^2 (Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York, p. 47). Twenty to thirty times the theoretical quantity of quinaldinic acid is required for the maximum colour development of ferrous quinaldinate. A quantity of potassium cyanide, at least 350 times that of ferrous iron present, is required for maximum intensification of the colour of the complex system. The coloured complex in the cyanide system is quite stable at room temperature and remains almost unchanged for about 24 hours. The sensitivity of the coloured cyanide system is almost four times greater than that of the pure ferrous quinaldinate system in solution.

Wave-length of Absorption Maximum and Influence of p_H on the Coloured System.—In a small dry beaker, 10 c.c. of ferrous ammonium sulphate (50 p.p.m.) containing hydroxylamine hydrochloride (1%) was taken along with 10 c.c. of quinaldinic acid (1%) solution in water. The p_H of the mixture was adjusted approximately by the addition of a dilute sodium bicarbonate solution. The volume of the solution was then made up to 50 c.c. with distilled water and the p_H carefully determined by the p_H-meter. A number of solutions having different p_H values could thus be prepared.

A solution of p_H 6, which was quite strongly coloured, was employed for determining the absorption maximum which was found to lie at 500 mμ. The optical densities of a number of solutions at different p_H were then measured at 500 mμ (Fig. 1). The maximum intensity of the coloured complex lies between p_H 5.8 and 7. There is little difference in λ_{max} though the intensity increases nearly 4 times with an excess of potassium cyanide.

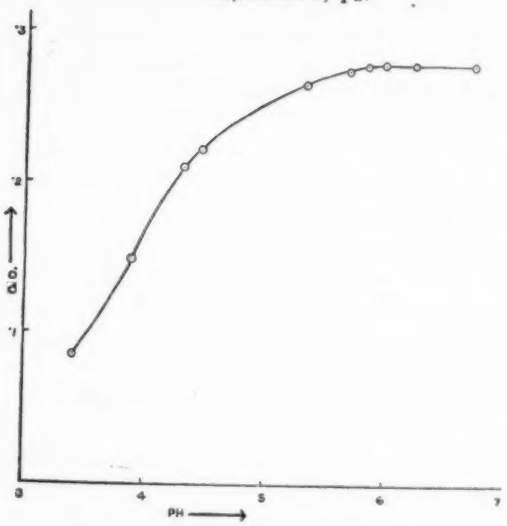
It should be stated here that in every case the measurements of optical density were made immediately after the preparation of the solution in order to avoid the risk of any turbidity appearing from the separation of ferrous quinaldinate. The colour formation was instantaneous. The solutions of ferrous salt or of the reagent have little or no absorption at or about 500 mμ. All the optical density measurements were made against water blank.

Beer's Law.—The coloured complex of ferrous quinaldinate with or without cyanide obeys Beer's law.

Influence of Cyanide and Pyridine Concentration.—The effect of the concentration of pyridine on the coloured system is shown in Fig. 2.

FIG. 1

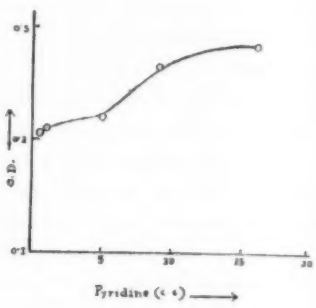
Influence of p_H.



Fe = 10 p.p.m. measured at 500 mμ.

FIG. 2

Effect of pyridine.



Ferrous amm sulph. 50 p.p.m. Fe containing $NH_2OH.HCl$ (1%), 10 c.c.; reagent 1% soln., 10 c.c.; total volume 50 c.c.; cell, 1 cm; 515 mμ.

With an increasing quantity of potassium cyanide p_H may rise up to 9, and with pyridine, up to 7. That the increase of colour intensity produced by potassium cyanide or pyridine is not due to this increase in p_H is clear from the values obtained under the same condition, as given below.

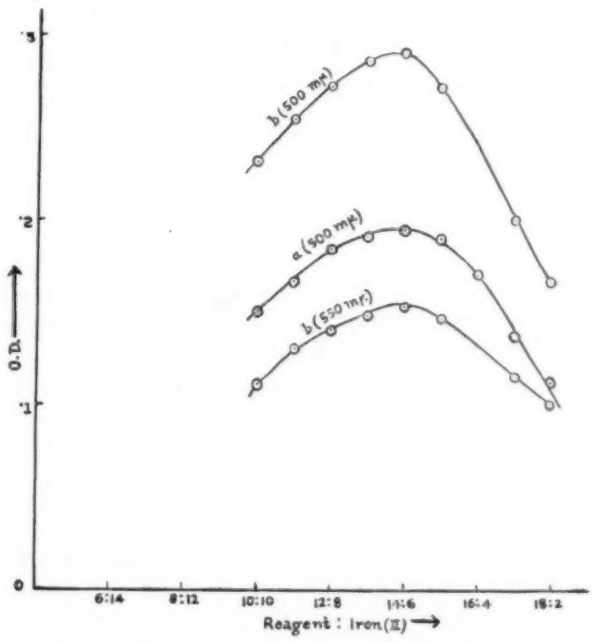
Optical densities of three different solutions containing the same quantity of ferrous ammonium sulphate (10 p.p.m.), $NH_2OH.HCl$ (0.2%) and quinaldinic acid (0.2%) were measured at 500 mμ. One of these solutions contained pyridine, another contained KCN, in quantities sufficient to make the p_H value of the solutions the same (5.3) as that of the solution without KCN or pyridine. The following results were obtained. Cell used was of 1 cm.

	O. D.
I. With no KCN or pyridine	0.265
II. With pyridine	0.278
III. With KCN	0.540

From a concentrated solution of ferrous salt and quinaldinic acid, pyridine gives a dark chocolate crystalline product. This was prepared by adding a solution of ferrous ammonium sulphate (1 g. in 20 c.c. water) to a solution of 2.5 g. of quinaldinic acid in the minimum quantity of water and then treating the mixture with 5 c.c. of pyridine. The chocolate crystalline precipitate separating was filtered, washed and dried in a vacuum desiccator over $CaCl_2$. {Found: Fe, 11.11; N, 8.95. $[Fe(C_{10}H_6O_2N)_2.(C_5H_5N)_2].2[Fe(C_{10}H_6O_2N)_2(C_5H_5N).H_2O]$ requires Fe, 10.82; N, 9.02%}.

Composition of the Coloured Complex of Ferrous Iron and Quinaldinic Acid.—The composition of the coloured complex in solution was determined spectrophotometrically by Job's method at p_H 5.99, with the use of sodium acetate—acetic acid buffer and in the presence of sufficient KNO_3 for maintaining a constant ionic strength. The optical density of the coloured solution gives a measure of the coloured complex in equilibrium. The values of measurements are shown in Fig. 3. The results show that the ratio of the coloured complex is 1 Fe : 2 acid.

FIG. 3



a. Ferrous ammonium sulphate *(0.004M)* containing NH_2OH HCl *(1%) x* c.c. ; quinaldinic acid *(0.004M) y* c.c. ; KNO_3 *(1M)* 10 c.c. ; buffer 18 c.c. ; total volume 50 c.c. ; cell 2 cm ; 500 mμ.

b. Ferrous ammonium sulphate *(0.005M)* containing $NH_2OH.HCl$ *(1%) x* c.c. ; quinaldinic acid *(0.005M) y* c.c. ; 500 mμ and 550 mμ ; other conditions same as in (a).

Instability Constant of the Coloured Complex

The instability constant of the coloured complex can be derived from its dissociation in solution according to the equation :

$$FeQ_2 \rightleftharpoons Fe^{2+} + 2Q^-$$

$$K = \frac{[Fe^{2+}] \times [Q^-]^2}{[FeQ_2]} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

(where QH = a molecule of quinaldinic acid and Q^- = a quinaldinate ion; [ ] denotes concentration).

As the ionic strength of the solutions was maintained at a constant value by the addition of potassium nitrate and as the solutions of the reactants employed were very dilute, the activities of the various constituents may be considered to remain unchanged and may be substituted by molar concentrations. The values of $[Fe^{2+}]$, $[Q^-]$ and $[FeQ_2]$ in the equilibrium system can be calculated from the following equation :

$$[Q_t] = [QH] + [Q^-] + 2\,[FeQ_2] \qquad \ldots (2)$$

(total reagent)

$$K_a = \frac{[Q^-] \times [H^+]}{[QH]} \qquad \ldots (3)$$

(where K_a = acid dissociation constant of QH)

$$[Fe_t] \text{ (total iron)} = [Fe^{2+}] + [FeQ_2] \qquad \ldots (4)$$

Now from the equations (2) and (3) the value of $[Q^-]$ can be calculated. Putting this value to equation (1) we get,

$$K_c = \frac{[Fe^{2+}]}{[FeQ_2]} \cdot \frac{K_a^2 \{ [Q_t] - 2\,[FeQ_2] \}^2}{\{ K_a + [H^+] \}^2} \qquad \ldots (5)$$

$[FeQ_2]$ is known from optical density measurements. $[Fe_t]$ and $[Q_t]$ are known. $[Fe^{2+}]$ may be obtained from equation (4). $[H^+]$ is obtained from p_H measurement, and the value of K_a at 25° is 1.1×10^{-5} (Wenger *et al.*, *loc. cit.*).

Table I (A, B) records the results of measurement of optical densities of the solutions studied.

TABLE I

A. Ferrous ammonium sulphate (0.002 *M*) containing $NH_2OH.HCl$ (1%) = *x* c.c. Quinaldinic acid (0.004 *M*) = *y* c.c. KNO_3 (1 *M*) solution = 10 c.c. Buffer (p_H 5.99) = 18 c.c. Total volume = 50 c.c. Cell-2 cm ; 500 mμ. Temp. = 25° (room temp.).

Fe-soln.	Quinaldinic acid.	O. D. at 500 mμ.
14 c.c.	6 c.c.	0.094
13	7	0.115
12	8	0.130
10 (a)	10	0.148
8 (b)	12	0.165
6 (c)	14	0.157

B. Ferrous ammonium sulphate (0.002 *M*) containing $NH_2OH.HCl$ (1%) = *x* c.c. Quinaldinic acid (0.005 *M*) = *y* c. c. Other conditions are same as in A.

Fe-soln.	Quinaldinic acid.	O.D. at 500 mμ.
13 c.c.	7 c.c.	0.147
12	8	0.162
10 (d)	10	0.175
8 (e)	12	0.195
6 (f)	14	0.170
5	15	0.159

Now, from Table I, the values of K_c for a, b, c, d, e and f are calculated according to equation (5) and the results recorded in Table II, wherefrom the instability constant for the ferrous quinaldinate complex is found to be 3.63×10^{-6}.

TABLE II

$K_a = 1.1 \times 10^{-5}$. $[H^+] = 0.1023 \times 10^{-3}$.

No.	[Q'].	[FeQ_2].	[Fe^{2+}].	K_c'.
a	8.00×10^{-4}	4.82×10^{-5}	3.52×10^{-4}	3.03×10^{-6}
b	9.60×10^{-4}	5.36×10^{-5}	2.65×10^{-4}	3.02×10^{-6}
c	1.12×10^{-3}	5.11×10^{-5}	1.89×10^{-4}	3.21×10^{-6}
d	1.00×10^{-3}	5.69×10^{-5}	3.43×10^{-4}	3.96×10^{-6}
e	1.20×10^{-3}	6.35×10^{-5}	2.57×10^{-4}	3.90×10^{-6}
f	1.40×10^{-3}	5.53×10^{-5}	1.85×10^{-4}	4.66×10^{-6}

Hence K_c (mean) = 3.63×10^{-6}.

DEPARTMENT OF INORGANIC CHEMISTRY,
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
CALCUTTA-32.

Received December 12, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

DEPENDENCE OF ELECTROKINETIC POTENTIAL ON THE DIELECTRIC CONSTANT OF THE MEDIUM. PART I. THE GLASS SYSTEM

By S. N. Mukherjee and S. Chatterjee

The influence of the dielectric constant of the medium on the zeta potential has been studied by the endosmotic technique in the glass system. Results appear to show an over-all diminution with decreasing dielectric constant, although the variations do not appear to be smooth in all cases.

Since Helmholtz's theory of double layer was proposed for explanation of the cataphoretic mobility of colloidal particles in an electrical field or more generally for the origin of electrical potential at the phase boundary, the dielectric constant of the medium, specially in the region of the double layer, was regarded as an important influencing factor from theoretical considerations. The dielectric constant has been invoked for explaining many observations connected with the coagulation or stability of colloids (cf. Freundlich, "Colloid and Capillary Chemistry", 1929). But a straight-forward investigation into the relationship of the dielectric constant and the zeta potential from the experimental side has not been paid so much attention as it deserves, as will be evident from the recent literature.

Present work has been undertaken with a view to assessing the role of the dielectric constant of the medium on the magnitude of the zeta potential by a straight-forward and direct experimentation. For this reason the electrokinetic potential was measured by the endosmotic method with a number of diaphragms of different materials and of different dielectric constants, prepared by mixing soluble organic liquids in water in different proportions.

Measurement of electrokinetic potential in a porous medium, made of fine particles, in contact with non-aqueous or aqueous—non-aqueous media, has recently been carried out by a few workers. The difficulty of such measurements lies in the fact that the correction for surface conductances in diaphragms is much more difficult than in capillaries made of the same material.

Coehn and Raydt (*Ann. Physik*, 1909, **30**, 777) compared the electro-osmotic velocity of different liquids through glass capillaries, but their results largely differed from those of some earlier as also of some later workers like Fairbrother and Balkin (*J. Amer. Chem. Soc.*, 1931, **53**, 389, 1564), Strickler and Mathews (*ibid.*, 1922, **44**, 1947), Perrin (*J. chim. phys.*, 1904, **2**, 607 ; 1905, **3**, 50) and De Smet and Delfoose (*Medikal. Koaickal. Vlaam, Akad. Wetenschap. Belg. Klasse Wetenschap.*, 1942, **4**, No. 10). The exact values of the electrokinetic potential in media of organic liquids of moderate dielectric constant, such as acetone, methyl alcohol,

etc., have been carefully measured recently by Rutgers *et al.* (*Trans. Faraday Soc.*, 1952, **48**, 635) in glass capillaries. Verwey (*Rec. trav. chim.*, 1942, **60**, 625) made some study on the electro-osmosis through diaphragms with non-aqueous liquids, but in his experiments, surface conductance appeared not to have been taken into account.

The present communication embodies the results of experiments on electro-osmosis in diaphragms made of glass. The media used were mixtures of methyl alcohol and water and ethyleneglycol and water in different proportions. Lithium chloride or sodium nitrate at a relatively high concentration was used for elimination of surface conductance in these experiments. The dielectric constant and viscosity of these mixtures were measured side by side and the endosmotic mobility correlated with the dielectric constant.

Experimental

Methyl alcohol, ethyleneglycol and lithium chloride used in these experiments were all of E. Merck's "Extra Pure" quality. The glass used for the diaphragm was obtained by pulverisation of pyrex glass into 150 to 200 mesh and sieved through standard sieves. The powdered glass used was washed with equilibrium water (sp. conductance 1.85×10^{-6} mho at 35°) several times till the conductance of the wash water showed no change on keeping in contact with the powder. Lithium chloride solution of sufficient concentration was also prepared with the same water. All experiments were performed at a temperature of $35° \pm 0.1°$.

Endosmotic experiments were carried out with the same apparatus as designed by Briggs *et al.* (*J. Phys. Chem.*, 1918, **22**, 256) and recommended by Mukherjee and Basu (this *Journal*, 1927, **4**, 461) and reported in details by Ghosh and Ray (*ibid.*, 1939, **16**, 634). Temperature in all measurements (endosmosis, viscosity, or dielectric constant) was maintained at $35° \pm 0.1°$ by an electrically controlled thermostat.

Measurement of dielectric constant was carried out by the heterodyne beat method. The apparatus with a piezo-electric quartz crystal (3 m.c.) oscillator was locally designed and made to order by a local firm. The apparatus was first calibrated and tested for its performance by checking the dielectric constants of a large number of known and standard liquids dielectric constants of which were accurately known. The accuracy of measurements was found to be within 1%.

The zeta potential was calculated from the endosmotic mobility of the bubble in cm/sec./unit potential gradient by the help of the equation

$$\zeta = \frac{4\pi\eta_1\kappa v}{Di} \times (300)^2 \text{ volts}$$

where, η_1 = viscosity coeff., v = vol. of liquid flowing per sec., κ = sp. conductivity, D = dielectric constant and i = current in amp. Results are recorded in the following tables

TABLE I

Glass diaphragm in alcohol-water mixture.

Temp. = 35°. LiCl = 0.14 *N*.

% EtOH by vol.	*D*.	η(poise).	ζ(mv.).	% MeOH by vol.	*D*.	η (poise).	ζ (mv.).
0	76.00	0.00721	54.13	0	76.00	0.00721	54.13
10	74.30	0.00955	48.72	10	74.30	0.00859	57.18
20	68.40	0.01285	44.18	20	69.21	0.00956	54.83
30	60.78	0.01426	41.59	30	64.98	0.01078	49.17
40	56.50	0.01568	52.14	40	60.74	0.01166	48.88
50	50.58	0.01607	55.51	50	58.20	0.01158	36.39
60	44.65	0.01642	68.96	60	55.65	0.01160	38.90
70	38.72	0.01591	63.93	70	48.03	0.01015	30.28
100	27.27	0.01111	58.80				

TABLE II

Glass diaphragm in ethyleneglycol-water mixture.

Temp. = 35°. LiCl = 0.14*N*.

% Eth. glyc. by vol.	*D*.	η (poise).	ζ (mv.).	% Eth. glyc. by vol.	*D*.	η (poise).	ζ (mv.).
0	76.00	0.00721	54.13	50	59.89	0.02420	48.55
10	74.30	0.00929	46.34	60	55.65	0.03149	45.50
20	71.76	0.01180	54.21	70	51.00	0.04201	40.74
30	68.36	0.01508	49.55	80	49.73	0.05625	28.15
40	66.25	0.01920	44.28	90	44.22	0.07577	29.00

TABLE III

AgI *ppt. diaphragm in* EtOH-H_2O.

Temp. = 35°. $NaNO_3$ = 0.14*N*.

% EtOH.	*D*.	η (poise).	ζ (mv.).	% EtOH.	*D*.	η (poise).	ζ (mv.).
0	76.00	0.00721	59.70	50	50.58	0.01607	91.11
10	74.30	0.00955	86.14	60	44.65	0.01642	89.32
20	68.40	0.01285	91.52	70	38.72	0.01591	89.16
30	60.78	0.01426	117.10	80	34.47	0.01541	89.45
40	56.50	0.01568	120.10	90	30.00	0.01331	99.23

DISCUSSION

Results indicate quite a marked effect of the dielectric constant of the medium on the ζ-potential. In the case of the glass diaphragm in ethyl alcohol—water

mixture, the ζ-potential at first diminishes with diminution of D, the dielectric constant, but beyond 40% of alcohol there has been a steady increase till at 70% it is observed to show some diminution at higher concentrations. The value in pure alcohol, however, comes up to a value almost equal to that in water (0% alcohol). In the case of methyl alcohol, however, there was a steady decrease in the value of the ζ-potential almost from the beginning up to 70% alcohol beyond which it was not possible to pursue further, as the results obtained were not found to be reproducible with direct and reverse currents. Such data have been rejected and only those which were found reproducible, both in the direct and reverse currents as well as by repetitions of the experiments at least thrice (and in some cases at least five times), have been shown in the table. The cause of the appearance of such irreproducibility could not be properly understood. It might be due to some disturbing effect appearing with increase in the concentration of methyl alcohol. With ethyl alcohol, the values of ζ-potential began to increase again when the dielectric constant diminished from 60.78 to 56.50 (with alcohol conc. 40% to 50%), but with methyl alcohol no such thing was observed. A continuous decrease persisted all through till the value of zeta reached as low a value as 30.28. These data are more or less in agreement with some of Rutger's observations, which were made in some other connections.

With ethyleneglycol, there has been a similar behaviour as in methyl alcohol in the fact that the observations could not be pursued beyond 90% concentration of glycol. At 90% a slight irreversibility appears, but it is extremely small and the data presented here are the outcome of five to ten repetitions. Only in the case of 40% glycol, there has been some anomaly which has also been confirmed by repetition and checking up of the data for 30% and 50% (one preceding the anomalous datum and the other succeeding it but since the sequence was observed to be the same in every case) the data have been presented from their mean values.

Owing to the difference in behaviour observed in the case of glass diaphragms, the whole set of experiments were repeated in the case of silver iodide diaphragm with media of varying dielectric constants. Only the data for ethyl alcohol and water mixture have been presented in Table III. Data for methyl alcohol or glycol and water are very much similar and have not been presented here for economy of space. Results show an initial increase but later on, a slight decrease has also been noticed to occur, followed again by further increase. Behaviours with methyl alcohol and glycol are also similar.

From the behaviour of glass diaphragms in different media, it was suspected that the actual behaviour might be due to the ionic activity. According to Debye-Hückel's law, the activity coefficient is given by

$$\log f = - AZ_+ Z_- \sqrt{\mu} + C\mu$$

where A is a constant depending on the dielectric constant and temperature, C, the salting out constant and μ, the ionic strength. In the present experiments where μ is kept constant by using LiCl or $NaNO_3$ of the same concentration, as in the

case of the glass diaphragm with methyl alcohol and ethyleneglycol, the same dielectric constant yields the same value of zeta, specially at lower concentrations of the non-electrolytes. At higher non-electrolyte concentrations, however, a slight divergence begins to appear. It appears that at lower percentages of the non-aqueous liquids, the constant A is the decisive factor, but at higher concentrations, the salting out constant C comes into prominence. Most prabably owing to this reason the data at higher alcohol concentrations show erratic behaviour so far as their reversibility is concerned.

Therefore it appears that the activity coefficient of ions, as normally expected, would exert influence on the value of ζ-potential. Variation of the dielectric constant influences the value of A in the Debye-Hückel expression for the activity coefficient, and this affects the values of zeta. At higher percentages of the non-electrolyte, the value of C (the salting out constant) is probably also influenced owing to the change in the nature of the medium, and the behaviours at higher concentrations of alcohol do not tally with those at lower concentrations.

The point is interesting and deserves intensive investigation. Further work is being done with different systems and more non-aqueous media. Results will be published in future communications.

PHYSICAL CHEMISTRY LABORATORIES,
JADAVPUR UNIVERSITY,
CALCUTTA-32.

Received January 10, 1958

[Jour. Indian Chem Soc , Vol. 35, No. 5, 1958]

THE φ-SCALE OF POTENTIAL AND ITS APPLICATION TO SOME ELECTROCHEMICAL PROBLEMS. PART I. THE NULL-POINTS OF METALS AND THE DEFINITION OF THE φ-SCALE OF POTENTIALS

By L. I. Antropov

A brief summary of the methods for the determination of the values of zero charge potentials of metals ($\epsilon_{q=0}$) has been given. The most reliable values of $\epsilon_{q=0}$ have been collected and tabulated. The scale of φ-potential has been described, in which every value of potential (ϕ) is given in relation to the corresponding value of $\epsilon_{q=0}$. The physical meaning of the φ-potential and its relation to the charge of metal, to the structure of electrical double layer and to the ion-exchange current have been considered.

At the beginning of this century it was shown that the maximum of electrocapillary curve corresponded to the uncharged surface of metal. The assumption was made that in this case the potential of mercury related to the solution was also equal to zero, and the dropping mercury electrode was therefore chosen as a base for the so-called "absolute potentials" of metals. The values of these "absolute potentials" were tabulated and given in many reference books. It was Frumkin who proved the invalidity of this proposition. Frumkin* and his school used to refer to the potential of the maximum of electrocapillary curve as "the potential of zero charges of metal ($\epsilon_{q=0}$)", or as a "null-point of metal". At present there are several methods for determining $\epsilon_{q=0}$-values, which have been elaborated by many investigators, and especially by Frumkin and his collaborators.

In this paper it is impossible to go into detailed consideration of these methods but it is quite necessary to discuss them in brief.

(*i*). *The Method of Electrocapillary Curves**.—In this method the null-point of metal is identified with the potential at the maximum of electrocapillary curve, obtained in a solution devoid of any surface-active particles. This method is applicable in the case of liquid metals such as mercury, gallium, amalgams**, and it has been successfully used also in estimating the null-points of different molten metals in contact with molten salts (Karpatchew *et al.*, *J. Phys. Chem. USSR.*, 1936, **7**, 754 ; 1937, **10**, 739 ; 1944, **17**, 47 ; 1948, **22**, 521, 1949, **23**, 453 ; *Acta Physicochim.*, 1940, **12**, 583 ; 1942, **16**, 331 ; *Z. physikal. Chem.*, 1936, **A176**, 182).

(*ii*). *The Method of Contact Angle.*—In this method the null-point of metal is estimated by measuring the contact angle (θ) between the gas or oil bubble and the metal, both immersed in the same solution, and by plotting the values of θ against the potential of the metal (Möller, *Z. physikal. Chem.*, 1908, **65**, 226 ; Frumkin *et al.*,

*For bibliography see : Frumkin, *Ergebn. exact. Naturweiss.*, 1928, **7**, 235, and Parsons in Bockris-Conway, "Modern Aspects of Electro-chemistry", 1954, London.

** The modification of this method in which the surface tension is calculated form the weight of given number of drops was used for determining the $\epsilon_{q=0}$-values of unstable amalgams (Antropov *et al.*, *Trans. Novotcherkassk Polytech. Inst.*, 1956, **34/48**, 63, 69).

Phys. Z. Sowjet., 1932, **1**, 225 ; 1934, **5**, 418 ; Actualities Sci. Industr., Paris, 1937, N373 ; Ukshe and Levin, *Compt. rend. Acad. Sci. USSR.*, 1955, **105**, 113). This method is applicable to metals with clean and smooth surface.

(*iii*). *The Surface Hardness Method.*—In this method the value of $\epsilon_{q=0}$ is identified with the potential corresponding to the extremum on surface hardness or external friction-potential curves (Rehbinder and Venstrom, *Acta Physicochim.*, 1944, **19**, 36 ; *Compt. rend. Acad. Sci. USSR.*, 1949, **68**, 325 ; *J. Phys. Chem. USSR.*, 1952, **26**, 12 ; Lücke and Mazing, *Z. Metallkunde*, 1951, **42**, 361 ; Bokris and Parry-Jones, *Nature*, 1953, **171**, 930). This method is applicable to solid metals.

(*iv*). *The Adsorption Method.*—In this method the null-point of metal corresponds to the value of potential at which there is no superfluous adsorption of acidic or alkaline compounds from the solution (Shlygin, Frumkin and Medvedovsky, *Acta Physicochim.*, 1936, **4**, 911 ; Frumkin and Shlygin, *ibid.*, 1936, **5**, 819 ; Kutchinsky, Burstein and Frumkin, *ibid.*, 1940, **12**, 795 ; Veselovsky, *ibid.*, 1939, **11**, 815). This method is especially useful in case of metals with a large specific surface.

(*v*). *Surface Charge Method.*—In this method it is assumed that the null-point of metal is equal to the potential at which the formation of a new area does not require any quantity of electricity for keeping the potential constant (Frumkin, *Z. physikal. Chem.*, 1923, **103**, 55 ; Bennewitz, *ibid.*, 1926, **124**, 115 ; Frumkin and Cirves, *J. Phys. Chem.*, 1930, **34**, 74 ; Grahame *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 2978 ; 1952, **74**, 1207). This method is applicable to liquid metals, but it can also be useful for the investigation of solid metals.

(*vi*). *The Electric Capacity Method.*—In this method the $\epsilon_{q=0}$ value is found from the position of the minimum on the curve : double layer capacity-potential (Proskurnin and Vorsina, *Compt. rend. Acad. Sci. USSR.*, 1939, **24**, 915 ; Vorsina and Frumkin, *ibid.*, 1939, **24**, 518 ; Borisova, Ershler and Frumkin, *J. Phys. Chem. USSR.*, 1948, **22**, 925 ; Borisova and Ershler, *ibid.*, 1950, **24**, 337). This method is applicable to different metals irrespective of their states.

(*vii*). *The Polarisation Curves Method.*—In this method the null-point of metal is associated with the bend of polarisation curve, which is due to the change of sign of the electrode surface (Lukovtcev, Levina and Frumkin, *J. Phys. Chem. USSR.*, 1939, **13**, 916 ; Kolotyrkin and Bune, *ibid.*, 1947, **21**, 581 ; Kolotyrkin and Medvedeva, *ibid.*, 1951, **25**, 1355 ; Antropov and Listopodov, *Trans. Novotcherkassk Polytech. Inst.*, 1956, **34/48**, 87). This method can only give approximate values of $\epsilon_{q=0}$, shifted usually in the negative direction. It is only applicable when the overvoltage is connected with slow discharge of hydrogen ions or of some other charged particles.

(*viii*). *The Work Function Method.*—In this method the value of $\epsilon_{q=0}$ is calculated from the corresponding value of work function (γ_e) by means of the semi-empirical equation

$$\epsilon_{q=0} = a - b\gamma_e \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where a and b are empirical constants (Vasenin, *J. Phys. Chem. USSR.*, 1953, **27**, 878). Equation (1) is based on the assumption of a simple relation existing between the

difference of null-points of two metals and their Volta-potential (Frumkin and Gorodetzkaja, *Z. physikal. Chem.*, 1928, **136**, 451).

With the methods (*iv*), (*v*) and (*vi*), the most reliable values of $\epsilon_{q=0}$ can be obtained. But while using the method (*vi*), it is necessary to consider that the values of $\epsilon_{q=0}$ found for solid metals will be sufficiently accurate only when the surfaces of the metals are smooth and homogeneous.

Fairly accurate data have been obtained for many molten metals by means of method (*iv*). It will be of interest to compare these data with the values of $\epsilon_{q=0}$ obtained for aqueous solutions. The results of this comparison are shown in Table I.

TABLE I

Comparison of $\epsilon_{q=0}$ values by different methods and under varied conditions.

Metal.	Electrolyte.	Temp.	Method.	$\epsilon_{q=0}$.
Tl	A*	420°	(*i*)	−0.74 volt
Tl	$10^{-3}N$-KCl	20°	(*vi*)	−0.82
Tl	$1N$-Na_2SO_4	20°	(*iii*)	−0.69
Cd	A*	450°	(*i*)	−0.72
Cd	$5\times10^{-3}N$-KCl	20°	(*vi*)	−0.90
Cd	,, ,,	20°	(*iii*)	−0.70
Pb	A*	450°	(*i*)	−0.66
Pb	—			−0.64
Zn	A*	450°	(*i*)	−0.62
Zn	$1N$-Na_2SO_4	20°	(*iii*)	−0.49
Ga	A*	450°	(*i*)	−0.60
Ga	$1N$-KCl, 0.1-N HCl	40°	(*i*)	−0.19
Mg	Solutions, melts	—	Diff. methods	−0.21
Ag	A*	1050°	(*i*)	−0.40
Ag	$0.1N$-KNO_3	20°	(*iv*)	−0.05
Te	A*	550°	(*i*)	−0.59
Te	$1N$-Na_2SO_4	20°	(*iii*)	−0.60

*By A is indicated the entectic mixture of LiCl and KCl.

It is evident that the values of $\epsilon_{q=0}$ obtained by different methods are in fair agreement. By comparing the $\epsilon_{q=0}$-values for aqueous solutions and for molten salts, an assumption has been made (Antropov, *Trans Novotcherkassk Polytech. Inst.*, 1954, **25/39**, 5) that the null-point of mercury does not depend on the nature of the solvent and does not change with temperature. The validity of this assumption follows from Table I where all the values of $\epsilon_{q=0}$, except those for silver, are approximately the same in molten salts and in aqueous solutions. It means that the role of adsorption of polar water molecules is of no great importance. The data obtained in molten salts can therefore be used for aqueous solutions, and *vice versa*. The sudden variation of the value of $\epsilon_{q=0}$ for silver is presumably due to interaction between silver and molten halide salts.

The results obtained by means of method (*viii*) and some other methods have not been included in Table I. Although the method (*viii*) offers a possibility of calculating $\epsilon_{q=0}$ for nearly all metals, this method is not sufficiently reliable in view of the fact

that most of the values of φ_e as obtained at present are far from being highly accurate. This method therefore can only be used in those cases where there are no experimental data available.

Some of the values of $\epsilon_{q=0}$, as estimated by the above methods, are collected in Table II. The majority of them are average or the most reliable experimental quantities. For ferrous metals, only the $\epsilon_{q=0}$ values were calculated by means of the equation (Antropov, *Uspechy Chimii, USSR.*, 1956, **25**, 1043):

$$\epsilon_{q=0} = -4.21 + 0.88\varphi_e \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

the most accurate data being used for φ_e (Tsarev, "Contact Potentials", USSR., 1949; Sachtler, *Z. Electrochem.*, 1955, **59**, 119).

TABLE II

*List of null-points of metals.**

Metal ...	Na/Hg**	Tl	Cd	Pb	Zn	Ga
$\epsilon_{q=0}$ (volts) ...	−1.79	−0.82	−0.72	−0.67	−0.64	−0.60
Metal ..	Co	Cr	Zn/Hg **	Al	Tl/Hg **	Sn
$\epsilon_{q=0}$ (volts) ...	−0.51	−0.45	−0.46	−0.40	−0.36	−0.34
Metal ...	Cd/Hg **	Hg	Cu/Hg **	Hg	Fe	Cu
$\epsilon_{q=0}$ (volts) ...	−0.34	−0.19	−0.18	−0.05	0.02	+0.10
Metal ...	C_{act} Ni	Pt/H	Te	Pt/O		
$\epsilon_{q=0}$ (volts) ...	+0.20,+0.21	+0.25	+0.60	~1.0		

*The list of values for several metals has also been given by Frumkin (*J. Phys. Chem. USSR.*, 1934, **5**, 240), by Parsons (*loc. cit.*) and by Antropov (*loc. cit.*).

**The data correspond to 0.01 in terms of the molal fraction of metal in amalgam. Within certain limits of concentration, the relation of $\epsilon_{q=0}$ of amalgams to their composition can be given by equation,

$$n/n_E \ \epsilon_{q=0} = \text{const} \pm \delta \log N_{Me} \quad \ldots \quad \ldots \quad (3)$$

(see Smirnova, Smirnov and Antropov, *Trans. Novotcherkassk Polytech. Inst.*, 1936, **34**/**48**, 69).

The potentials used by electrochemists are generally given against some reference electrode, very often *versus* normal hydrogen electrode (hydrogen scale of potentials). All the values of $\epsilon_{q=0}$ in Table II are also given in hydrogen scale (ϵ-scale). This scale, though very useful in thermodynamical treatment of electrochemical system, is at the same time not so convenient in solving the kinetics problems of electrochemistry. The hydrogen scale as well as other scales, based on some reference electrode, cannot give any information regarding the charge of the metal in relation to the solution. The value and the sign of the ϵ-potential show only the relation of the electrode under investigation to the reference electrode. The fact that the ϵ-potentials of different metals in equilibrium with solutions of their salts are equal, does not mean that the charges of these two metals are the same; it only indicates that they are in equilibrium with one another.

In many cases another scale, in which the null-point of metal is chosen as the basis, is more suitable (Antropov, *J. Phys. Chem. USSR.*, 1951, **25**, 1494). It is

obvious that in this scale each value of potential (φ) represents a difference between the potential of the electrode under given conditions and the corresponding value of $\epsilon_{q=0}$. Thus, the standard potential of the metal in this new scale will be:

$$ {}_M\varphi^0 = {}_M\epsilon^0 - {}_M\epsilon_{q=0} \quad \ldots \quad \ldots \quad \ldots \quad (4) $$

For example:

$$ {}_{Zn}\varphi^0 = {}_{Zn}\epsilon^0 - {}_{Zn}\epsilon_{q=0} = -0.76 - (-0.64) = -0.12V \quad \ldots \quad (5) $$

To elucidate the physical meaning of the potential in this scale, hereafter indicated as φ-scale, consider the system: M/S/M′/M″.

The E.M.F. (E) of this system will be given by the formula:

$$ E = {}^M\Delta^{M''}\varphi + {}^M\Delta^S\varphi + {}^S\Delta^M\varphi \quad \ldots \quad \ldots \quad (6) $$

where φ's are the values of so-called inner potentials of corresponding phases (Lange, *Z. Elektrochem.*, 1951, **55**, 26; Parsons, *loc. cit.*).

The ${}^M\Delta^{M'}\varphi$, *i. e*, the difference of inner poientials of two metals M and M′, is equal to the Galvani potential. The ${}^M\Delta^S\varphi$ is the difference of inner potentials of metal M and solution S. On the other hand,

$$ {}^M\Delta^S\varphi = {}^Mg^S_{ion} + {}^Mg^S_{dip} \quad \ldots \quad \ldots \quad (7) $$

where g_{ion} is a result of the ionic transition through the metal—solution interface and g_{dip} is due to the oriented adsorption of polar molecules at the same interface. A similar equation will be valid for ${}^S\Delta^{M'}\varphi$, hence,

$$ E = {}^M\Delta^{M''}\varphi + {}^Mg^S_{ion} + {}^Sg^{M'}_{dip} + {}^Sg^{M'}_{dip} \quad \ldots \quad \ldots \quad (8) $$

It will be assumed that the E.M.F. of this system is equivalent to φ-potential of metal M′, *i.e.*

$$ E = {}_{M'}\varphi \quad \ldots \quad \ldots \quad (9) $$

But in this case all the three metals M, M′ and M″ are of the same nature and composition and, hence, the ${}^M\Delta^{M'}\varphi$ will be equal to zero. Moreover, one of the two samples of the same metal placed under conditions corresponding to a potential equals to the null-point of this metal; therefore ${}^Mg^S_{ion}$ will also be equal to zero, and

$$ {}_{M'}\varphi = {}^Sg^{M'}_{ion} + {}^Sg^{M'}_{dip} - {}^Sg^{M}_{dip} \quad \ldots \quad \ldots \quad \ldots \quad (10) $$

It means that the potential of a metal, given in φ-scale, is a measure of its charge and of the change of character and degree of dipoles orientation on the metal—solution interface. From equation (10) it is evident that ${}_{M'}\varphi$ can be equal to zero in two cases: (1) when the value of ${}^Sg^{M'}_{ion}$ is equal to zero and ${}^Sg^{M'}_{dip}$ is equal to ${}^Sg^{M}_{dip}$; this corresponds to the conception of null-point of metal which is used in this paper; (2) when the value of ${}^Sg^{M'}_{ion}$ is compensated for by the difference $({}^Sg^{M'}_{dip} - {}^Sg^{M}_{dip})$. These conclusions are of some interest in connection with the discussion on Lippmann's and Billitzer's potentials (*Z. Elektrochem.*, 1955, **59**, 818). It is also evident that the value and the sign of φ-potential stand in close relation to the structure of electrical double layer on the metal—solution interface. This is shown in Fig. 1 which

gives a somewhat simplified picture of the double layer for the two cases: (*a*) $\varphi > 0$ and (*b*) $\varphi < 0$. As is seen from Fig. 1, if $\varphi < 0$, the discharge and the ionisation of metallic ions in the presence of foreign cations will be retarded due to the adsorption of the latter on the metal-solution interface. On the contrary, when $\varphi > 0$, the adsorption of anions will accelerate the process of ion exchange between these two phases. Therefore, the exchange current corresponding to the equilibrium state of metal-solution system ought to have some functional connection with φ-potential.

FIG. 1

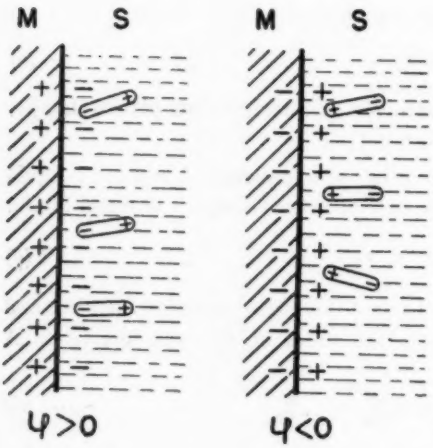
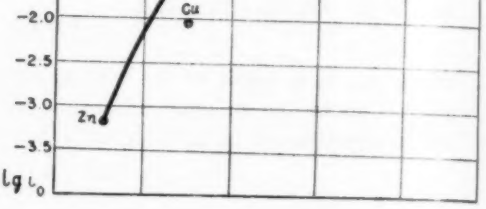


FIG. 2



There are very few experimental data to prove this suggestion, but Fig. 2 corroborates it. In drawing this picture we have used the values of exchange currents obtained by Randles and Somerton (*Trans. Faraday Soc.*, 1952, **48**, 951) for dilute amalgams in contact with solutions containing the salt of the corresponding metal and an excess of foreign electrolyte*. The values of $\epsilon_{q=0}$ were calculated on the strength of the supposition that the concentration of metal atoms in amalgams was the same (1×10^{-3} *N*) as that of metal ions in the solution, the data for $\epsilon_{q=0}$ being those obtained by Smirnova, Smirnov and Antropov (*loc. cit.*). The value of the velocity of ion exchange for mercury was taken from a paper by Rosental and Ershler (*J. Phys. Chem. USSR.*, 1948, **22**, 1944).

It is therefore natural to expect that the value of φ-potential should play an important role in all rate electrochemical processes. Other papers of this series will be devoted to this problem.

The author wishes to record his sincere thanks to Prof. S. K. Bhattacharyya, Applied Chemistry Department, for his interest in the work.

*The data for Bi have not been included in Fig. 2 because we have no values of $\partial i/\partial \epsilon_{q=0}$ that may be relied upon.

DEPARTMENT OF APPLIED CHEMISTRY,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

Received October 18, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

STABILITY AND ELECTROKINETIC POTENTIAL OF ALUMINIUM OXIDE HYDROSOL

By B. N. Ghosh and D. K. Chattoraj

In the region of slow coagulation, the apparant electrokinetic potential ζ_a of an Al_2O_3 sol has been measured both by the electro-osmotic and electrophoretic methods in the presence of equicoagulating concentrations of electrolytes containing counter ions of different valency. A plot of $1/\zeta_a$ against $1/S$ (where S represents the bulk specific conductivity of the supernatant liquid in equilibrium with the coagulum) yields a straight line in agreement with the equation

$$1/\zeta_a = 1/\zeta + m\frac{1}{S}$$

discussed in previous papers. From the intercept of the straight line on the $1/\zeta_a$ axis, the value of true ζ has been calculated. The results lead to the conclusion that a given rate of coagulation of the Al_2O_3 sol by different electrolytes is characterised by a definite value of the true ζ-potential, independent of the valency of the counter ions used.

The role of electrokinetic potential in determining the stability of colloids has engaged the attention of many investigators. Hardy (*Proc. Roy. Soc.*, 1900, **A**, **66**, 110) first suggested that a colloid coagulated when it was isoelectric with the dispersion medium. Powis (*Z. physikal. Chem.*, 1915, **89**, 188) on the basis of his own experiments and those of Ellis (*ibid.*, 1912, **80**, 597) put forward the theory of critical potential for coagulation of colloids. The experimental results on arsenious sulphide and silver iodide sols (*J. Chem. Soc.*, 1916, **109**, 734 ; *Kolloid Z.*, 1937, **78**, 32) do not seem to support this theory. In all these experiments, however, the ζ-potential has been calculated from the Smoluchowski equation, which according to various workers does not give the correct value of this potential owing to neglect of surface conductance and other factors.

According to Ghosh (this *Journal*, 1954, **31**, 273, 394 ; *Trans. Faraday Soc.*, 1954, **50**, 955) the electro-osmotic equation for a diaphragm, taking correction for surface conductance into account, is of the form

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + \frac{2\alpha\chi}{\zeta r}\cdot\frac{1}{S} \qquad \ldots \qquad \ldots \quad (1)$$

where ζ represents the true electrokinetic potential and ζ_a, the potential calculated on the basis of the Smoluchowski equation, r, radius of the capillary equivalent to the average pore of the diaphragm, χ, the specific surface conductance of the particles and S, the bulk specific conductance of the liquid ; α is a correction factor for diaphragm introduced by Ghosh (this *Journal*, 1955, **32**, 69, 402 ; *Naturwiss.*, 1955, **42**, 121).

For large values of κa, the electrophoretic equation of Henry (*Trans. Faraday Soc.*, 1948, **44**, 1021) and Booth (*ibid.*, 1948, **44**, 955) can be put in the form (Ghosh *et al.*, *Nature*, 1955, **176**, 1080)

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + \frac{\chi}{\zeta . a}\cdot\frac{1}{S} \qquad \ldots \qquad \ldots \quad (2)$$

where 'a' represents the radius of the particles ; κ is the characteristic term of the Debye-Hückel equation, the other terms having the same significance as before.

By utilising equations (1) and (2), given above, attempts have been made to measure the electrokinetic potential of aluminium oxide sol in the presence of comparable concentrations of electrolytes.

Experimental

The sol was prepared by adding a concentrated solution of ammonia dropwise with continuous stirring to a solution of aluminium nitrate, maintained at 70-80°. Addition of ammonia was stopped when the precipitate formed dissolved very slowly. Two litres of the sol, thus prepared, were dialysed for about three months and then stored in a stoppered Jena bottle where it was allowed to age for a month.

The aluminium oxide content of the sol was 4.1 g./litre and its p_H and specific conductance were 5.08 and 3.500×10^{-5} mhos respectively.

Determination of Equicoagulating Concentrations.—The electrolyte solution (2 c.c) was mixed with the sol (2 c.c.), left as such for 18 hours and then the mixture was centrifuged for 2 minutes at a definite speed. The supernatant liquid from the top was pipetted into a clean dry test tube and examined for turbidity or transparency. The concentration of electrolyte, which on addition to the colloid gave just a clear supernatant solution by the above treatment, was taken as its equicoagulating concentration.

Separation of the Coagula from the Supernatant Liquid.—The sol (40 c.c.), mixed with the electrolyte solution (40 c.c.) of equicoagulating concentration, was allowed to stand for 18 hours. The coagula were then separated from the supernatant liquid by centrifuging and were used for electro-osmotic experiments. The clear supernatant liquid was used for electro-osmotic as well as for electrophoretic experiments.

Electro-osmotic Experiments

The coagula, separated from the colloid-electrolyte mixture (40 c.c. of each), were transferred to a U-shaped tube which was then centrifuged at a given speed.

The volume of diaphragm in all cases was maintained constant as far as practicable by regulating the time of centrifuging. This ensured more or less the same degree of packing and the same average size of the pores when equicoagulating concentrations of different electrolytes were used so that z and r in equation (1) for endosmosis should remain constant. The two side-tubes of the U-tube were connected *via* pressure tubings and two three-way stop-cocks to a glass tube having a narrow uniform bore and four rectangular bends. The U-tube containing the diaphragm was filled with the supernatant solution, separated from the coagula, and clamped in a thermostat bath (35°). With the help of the two three-way stop-cocks, the bent tube was filled with water and an air-bubble of length of about 0.4 cm was drawn into it. The electric field was applied through the platinum black electrodes, immersed to a definite depth inside the two limbs of the U-tube. The liquid flowing through the diaphragm caused the air-bubble to move. From the rate of movement of the air-bubble, the current flowing through the U-tube, the specific conductance of the supernatant solution, the cross-section of the bent tube and other relevant data, ζ_a was calculated. The data are presented in Table I.

TABLE I

Temp. = 35°. ζ = 28.6 mv. $m = \frac{2\pi X}{\zeta . r} = 4.06 \times 10^{-6}$.

Electrolytes.	Equicoagulating conc.	Sp. cond. of supernatant soln. ($S \times 10^3$).	ζ_a Obs.	ζ_a Calc. from eq. (1).
NaCl	6.198×10^{-2} N	771.40 mhos	28.0 mv.	28.1 mv.
Na_2SO_4	9.324×10^{-4}	13.42	14.2	15.3
$K_3Fe(CN)_6$	4.209×10^{-4}	4.943	8.5	8.5
NaCl	2.066×10^{-4}			
&	&	7.771	11.5	11.4
$K_3Fe(CN)_6$	3.988×10^{-4}			

Electrophoretic Experiments

A modified form of Burton's U-tube apparatus was used for electrophoretic measurements. Each limb of the U-tube carried a stop-cock of wide bore, the cross-sectional area of which was the same as that of the limbs. The thistle funnel, the tube connecting it through a stop-cock to the bottom of the U-tube, and the entire lower part of the U-tube up to the upper level of the stop-cocks in the limbs were filled with the colloid-electrolyte mixture. The upper limbs were nearly filled with the clear supernatant liquid having the same conductance as that of the intermicellar fluid of the colloid-electrolyte mixture. The colloid-electrolyte mixture was prepared in the following way. The sol (20 c.c.) was mixed with 20 c.c. of the electrolyte of equicoagulating concentration and the mixture was allowed to stand for 30 minutes for attaining equilibrium and was then used in Burton's tube.

After the apparatus was fitted up in the way described above, small specially designed calomel electrodes were dipped into the supernatant liquid at the top of the U-tube. The level of the liquid in the two limbs was adjusted and the stop-cocks were opened. The stop-cock connecting the thistle funnel was also carefully opened so as to allow the colloid-electrolyte mixture to rise slowly in the limbs. When the colloid-liquid boundary stood at a level of about 2.5 cm above the stop-cocks, the flow from the thistle funnel was stopped by closing the stop-cock. The current was now switched on. It was regulated by an adjustable resistance and measured by a sensitive microammeter. The cross-sectional area 'A' of the limbs of the U-tube, where the boundary moved, was also determined. The potential gradient was found from the expression $i/A.K$, in which 'i' represents the current and K, the average of the specific conductances of the supernatant liquid and the colloid-electrolyte mixture.

After the upward movement of the boundary was observed, the colloid was found to coagulate slightly. So in order to measure the rate of downward movement, another similar experiment was carried out with fresh boundary, made of fresh colloid-electrolyte mixture and the supernatant solution. The current in this case was, however, allowed to pass in the reverse direction. Mean values of ζ_a for upward and downward movements are presented in Table II. The electrolytes used in electrophoresis always contained a small quantity of NaCl to ensure reversibility of the calomel electrodes.

TABLE II

$$\text{Temp.} = 28^\circ. \quad \zeta = 31.0. \quad m = \frac{\chi}{\zeta . a} = 2\ 198 \times 10^{-6}.$$

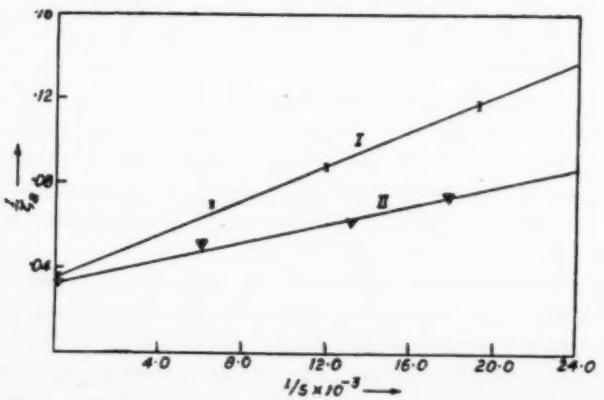
Electrolytes.	Equicoagulating conc.	Sp. cond. of supernatant solution ($S \times 10^5$).	Sp. cond. of colloid-electrolyte ($S' \times 10^5$)	ζ_a. Obs.	ζ_a. Calc from eq. (2).
NaCl	6.198×10^{-2} N	699.7 mhos	696.0 mhos	30.5 mv.	30.7 mv.
NaCl & Na_2SO_4	2.066×10^{-4} & 8.880×10^{-4}	14.49	14.20	19.6	21.0
NaCl & $K_3Fe(CN)_6$	2.066×10^{-4} & 3.988×10^{-4}	7.013	6.836	16.3	15.7
NaCl & $K_3Fe(CN)_6$	1.033×10^{-4} & 3.988×10^{-4}	5.625	5.374	13.6	13.6

In Fig. 1, the length of the vertical lines in the electro-osmotic curve I indicates the maximum range of variation of $1/\zeta_a$ in five different experiments.

DISCUSSION

It will be noticed from endosmotic data recorded in Table I and from curve I in Fig. 1, that a straight line is obtained when the reciprocals of ζ_a are plotted against reciprocals of the corresponding conductances of the supernatant solutions. Hence, it follows from equation (1) that ζ and m, and consequently χ (since m contains χ), for the sol remain constant at the equicoagulating concentrations of the different electrolytes used. The value of true ζ, found from the intercept on $1/\zeta_a$ axis, is 28.6 mv.

FIG. 1



An examination of the electrophoretic data in Table II (Fig. 1, curve II) also indicates that there exists a linear relationship between $1/\zeta_a$ and $1/S$ as is to be expected

from equation (2). This confirms the conclusion which we have already drawn from the electro-osmotic data. The value of true ζ, found from the intercept on $1/\zeta_a$ axis in the electrophoretic measurements, is 31 mv. The average of the values of ζ, found by the electro-osmotic and electrophoretic measurements, is 29.8 and this may be taken as the true ζ, potential of the Al_2O_3 sol in the presence of the equicoagulating concentrations of the electrolytes used by us. It may therefore be concluded that a given rate of coagulation of aluminium oxide sol is characterised by a definite value of the true ζ-potential, independent of the valency of the counter ions used.

PHYSICAL CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE &
TECHNOLOGY, CALCUTTA.

Received January 17, 1958.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

ESTIMATION OF FORMATES BY OXIDATION WITH MERCURIC CHLORIDE

By Sameer Bose

A specific method, applicable in presence of salts of other organic acids, is described for the volumetric and gravimetric estimation of formate ion. The precision of the volumetric method is 0.5% or more. An iodometric procedure, suitable for micro estimation of quantities as low as 1 mg. of formic acid, has also been evolved

Fuchs (*Z. anal. Chem.*, 1929, **78**, 125) determined neutral alkali formates by titration of the hydrochloric acid liberated during its oxidation with mercuric chloride.

$$HCOONa + 2\,HgCl_2 \longrightarrow NaCl + HCl + CO_2 + Hg_2Cl_2$$

Instead of using an indicator, Fuchs titrated with alkali to the appearance of a yellow precipitate of mercuric oxide. Oldeman (*Pharm. Weekblad*, 1931, **68**, 379) recommended titration to phenolphthalein end-point after adding sodium chloride to tie up the excess of mercuric chloride. The latter procedure was found to afford an error of 3-4%. The present communication describes a modification of the same, offering more precise results.

Experimental

Formic acid and sodium hydroxide used were of A. R. quality. Potassium iodide, sodium iodate, sodium acetate and mercuric chloride were of Merk's chemically pure variety. Standard solutions of sodium formate were prepared by neutralising formic acid solutions with CO_2-free NaOH solution in presence of phenolphthalein. As alcohol was found to interfere, dry crystals of the indicator were used. The CO_2 free alkali was prepared by Sörensen's strong alkali procedure (*Biochem. Z.*, 1909, **21**, 168) and stored in an aspirator fitted with sodalime tube. The standard solutions for micro-estimations were prepared by diluting the $N/10$ solutions 10 to 50 times with conductivity water.

Volumetric Estimation.—The neutral formate solution (20-25 c.c.) containing not more than 50 mg. of formic acid was pipetted into a 150 c.c. pyrex conical flask and treated with 10 c.c. of 15% sodium acetate (formate-free) solution. The air in the flask was as far as possible displaced by steam which was passed into it without actually bubbling through the solution. A saturated mercuric chloride solution (20 c.c., 7.1%) was quickly added and the flask closed with a rubber cork which was pressed in with a little force. Heating was carried out in an electrically heated water-bath by placing the flask in boiling water so as to immerse only its lower part containing the solution. Further, it was weighted by a band of lead which encircled its lower portion. As the flask developed a slight pressure, the bath was placed in a corner of a room, protected by flame guards, and left undisturbed except for the addition of water from time to time. The steaming was found to reduce

the pressure considerably and prevented blowing off of the cork. After half an hour's heating the bath was switched off and allowed to cool. The flask was finally cooled under the tap, its stopper removed and the contents boiled for half a minute by placing it on an electrical hot plate (pre-heated). The total period of heating on the hot plate was limited to 2 or 3 minutes during which time all the CO_2 was found to escape. The flask was again stoppered and allowed to cool when its contents were filtered through a sintered crucible (1G4), using about 40 c.c. of water for washing. The filtrate which was received in a 250 c.c. filter flask was treated with an excess of solid potassium iodide (4 g.) till the red precipitate first formed completely dissolved, and then it was titrated with 0.1*N*-NaOH solution to phenolphthalein end-point. The results of evaluation of six different solutions, carried out in duplicates, as recorded in Table I, revealed that the experimental values compared favourably with the actual ones and the error which was always on the lower side did not exceed 0.5 % (1 c.c. of 0.1*N* alkali corresponds to 4.6 mg. of formic acid).

TABLE I

Expt. No.	Formic acid (mg.) by				
		Volumetric.		Gravimetric.	
	Calc.	Found.	Error.	Found.	Error.
1.	50.5 mg.	50.3 mg.	−0.4%	50.1 mg.	−0.8%
2.	46.0	45.8	−0.5	46.1	+0.2
3.	42.2	42.1	−0.3	41.9	−0.7
4.	40.3	40.3	Nil	40.6	+0.8
5.	37.4	37.2	−0.5	36.9	−1.3
6.	36.1	36.0	−0.3	36.2	+0.3

Gravimetric Estimation.—The reaction was carried out in a manner similar to that described above. The white precipitate of mercurous chloride obtained was filtered through a weighed sintered crucible (G4) and repeatedly washed with about 100 c.c. of water and finally with 25 c.c. of acetone. The crucible was allowed to dry at room temperature (22°) by leaving it overnight, slightly inclined, on a clean table and then weighed. From the weight of mercurous chloride, the formic acid content was calculated. One gram of the chloride is equivalent to 97.45. mg. of formic acid. The results of gravimetric and volumetric estimations of the same aliquots are recorded in Table I.

Micro-estimation.—Neutral formate solution (1-10 c.c.) containing 1-5 mg. of formic acid was pipetted into a 150 c.c. pyrex conical flask. After displacing the air inside the flask by steam, a saturated mercuric chloride solution (20 c.c.) was quickly added and then it was closed with a good compressed bark cork. The flask was heated in boiling water in the manner already described. The gas pressure developed inside it was not much as only about 2 c.c. of CO_2 was produced during the reaction, which took considerable time (2-3 hrs.) as its velocity diminished with increase in H^+-ion concentration. After the reaction was over, the solution was cooled and filtered through a sintered crucible by applying a mild suction. Minimum quantity of

conductivity water was used for washing and transferring the filtrate to a 250 c.c. conical flask. The filtrate was treated with an excess of solid potassium iodide (4-5 g.) and sodium iodate (0.5 g.) and then left in the dark for 5 minutes for complete oxidation of the H^+ ions ($IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$). The solutions being very dilute, this process of oxidation was found to take a little time. Darkness was sought to prevent oxidation of potassium iodide ; a closed cupboard was found suitable for the purpose. The iodine liberated was finally titrated with 0.01*N* hypo solution taken in a 10 c.c. micro-burette, using 2 c.c. of 1% starch solution as indicator (1 c.c. of 0.01 *N* hypo solution ≡ 0.46 mg. of formic acid). The results of assay of six different solutions are recorded in Table II. The precision is about 1%, the error always occurring on the lower side.

TABLE II

Expt. No.	I_2 liberated. (0.01 *N*)	Formic acid. Present.	Found.	% Error.
1.	2.20 c.c.	1.012 mg.	1.012 mg.	Nil
2.	4.35	2.024	2.001	−1.1
3.	5.46	2.530	2.512	−0.7
4.	6.55	3.036	3.013	−0.8
5.	8.74	4.048	4.020	−0.7
6.	10.90	5.060	5.014	−0.9

CONCLUSION

The macro (volumetric) method has certain advantages as well as disadvantages. The procedure has the usefulness of being applicable in presence of salts of other acids, weak as well as strong. But its greatest drawback lies in the fact that it finally gives rise to a solution containing a mixture of carbon dioxide and acetic acid, out of which the former has to be completely driven off. If the heating is carried out longer than necessary, some acetic acid is also lost, while insufficient heating affords higher values due to the retention of some carbon dioxide. The micro procedure appears to be more elegant as it does away with this difficulty and also possesses a sharp end-point. But it has the disadvantage of being inapplicable in presence of salts of other weak acids which make the process of oxidation of the H^+ ions by IO_3^- and I^- ions incredibly slow and impracticable. Where high precision is not required, the gravimetric procedure will be found more suitable as it has none of the disadvantages mentioned above.

Sincere thanks of the author are due to Dr. V. Gore, Professor of Chemistry, for all the facilities.

DEPARTMENT OF CHEMISTRY,
MAHAKOSHAL MAHABIDYALAYA, JABALPUR.

Received February 2, 1958.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART III. LEAD ACETATO COMPLEXES AND LEAD PROPIONATO COMPLEXES

By S. K. Siddhanta and S. N. Banerjee

Bjerrum's method for determining the values of successive constants in step equilibria has been shown to be unsuitable in cases where the ligand is charged. Suitable modifications have been introduced to adapt Bjerrum's method in cases of charged ligand, taking into account the activity coefficients of the ions present in the solution, calculated by the application of the "Debye-Hückel limiting law" from the value of the ionic strength of the solution mixture.

The p_Hs of aqueous solution mixtures of lead acetate and nitric acid at different concentrations after attainment of equilibrium have been determined, and the data utilised to calculate the thermodynamic dissociation constants, K_1 and K_2, for the two successive equilibria,

$$PbA_2 \rightleftharpoons PbA^+ + A^- \text{ and } PbA^+ \rightleftharpoons Pb^{2+} + A^-$$

(where A stands for acetate or propionate ion), applying Bjerrum's method modified as above. The inapplicability of the Debye-Hückel limiting law to electrolyte solutions at finite concentrations has also been properly considered, and ingenious corrections have been made in finding the value of K_1 and K_2, which are 31.2×10^{-3} and 3.31×10^{-3} at 31-34.5° respectively for lead acetate and 51.1×10^{-3} and 4.57×10^{-3} at room temperature (21-30°) for lead propionate.

A complex of the type MA_2, where M is a bivalent metal ion and A is any ligand, may dissociate in aqueous solution in two stages, viz.,

$$MA_2 \rightleftharpoons MA + A \quad \ldots \quad \ldots \quad (A)$$

$$MA \rightleftharpoons M + A \quad \ldots \quad \ldots \quad (B)$$

The first and second dissociation constants of lead acetate are therefore given by

$$K_1 = \frac{a_{MA} a_A}{a_{MA_2}} = k_1 \cdot \frac{f_{MA} \cdot f_A}{f_{MA_2}} \quad \ldots \quad \ldots \quad (1)$$

and

$$K_2 = \frac{a_M \cdot a_A}{a_{MA}} = k_2 \cdot \frac{f_M \cdot f_A}{f_{MA}} \quad \ldots \quad \ldots \quad (2)$$

where k_1 and k_2 are the classical concentration constants given by

$$k_1 = \frac{c_{MA} \bar{c}_A}{c_{MA_2}} \quad \ldots \quad \ldots \quad (3)$$

and

$$k_2 = \frac{c_M \bar{c}_A}{c_{MA}} \quad \ldots \quad \ldots \quad (4)$$

Bjerrum ("Metal Ammine Formation in Aqueous Solution", P. Haase and Son, 1941) has developed a method of evaluating the successive mass action constants in step equilibria like (A) and (B); the method, however, is admirably suitable in cases where the ligand 'A' is a neutral molecule like NH_3, but not at all accurate in cases where the ligand 'A' is a charged ion like CH_3COO^- or $C_2H_5COO^-$.

Bjerrum defines formation function $\bar{n}$ in any solution mixture containing MA_2 and a strong acid as the average number of ligands per M^{2+} ion given by the following expressions,

$$\bar{n} = \frac{c_{MA^{2+}} + 2c_{MA_2^{2+}}}{c_{M^{2+}} + c_{MA^{2+}} + c_{MA_2^{2+}}}$$

$$= \frac{k_1 c_A + 2c_A^2}{k_1 k_2 + k_1 c_A + c_A^2} \quad \ldots \quad \ldots \quad (5)$$

Experimentally Bjerrum prepared two or more solution mixtures with different amounts of MA_2 and a strong acid keeping the total volume constant, and then determined for every such solution mixture, using some suitable method, the "free" ligand concentration, 'x', and $\bar{n}$ from the equation,

$$\bar{n} = \frac{\text{total ligand} - \text{free ligand}}{\text{total metal}} = \frac{2C - x}{C} \quad \ldots \quad (6)$$

'x' being the concentration of the ligand (not attached to the metal ion) present in the solution in the base form 'A' and in the acid form 'HA' ($x = c_A + c_{HA}$). Thus obtaining the values of $\bar{n}$ and c_A for any two solution mixtures, two simultaneous equations will be obtained from equation (5), the solution of which will give the values of 'k_1' and 'k_2'.

In cases where 'A' is neutral,

$$K_1 = k_1 \frac{f_{MA^{2+}} \cdot f_A}{f_{MA_2^{2+}}} = k_1$$

for solutions of low ionic strengths, since $f_A = 1$, and "$f_{MA^{2+}} = f_{MA_2^{2+}}$" by the Debye-Hückel limiting law.

Similarly, $$K_2 = k_2 \frac{f_{M^{2+}} \cdot f_A}{f_{MA_2^{2+}}} = k_2.$$

Evidently in such cases, the classical concentration constants and the thermodynamic constants are very nearly the same and, hence, the former can be regarded as constants, independent of the ionic strengths. Therefore equation (5), which is essentially a stoichiometric equation involving the classical constants 'k_1' and 'k_2', remains valid for two solutions of different ionic strengths *if the ligand is neutral.* Hence, the values of 'k_1' and 'k_2' can be obtained more or less accurately by solution of simultaneous equations, as indicated above.

If, however, the ligand is a charged ion like CH_3COO^- and $C_2H_5COO^-$, the thermodynamic constants, 'K_1' and 'K_2', and classical contsants, 'k_1' and 'k_2', have got very different values and, in fact, 'k_1' and 'k_2' cannot be regarded as constants for different

solution mixtures of varying ionic strengths. Equation (5) cannot therefore be employed to obtain the values of 'k_1' and 'k_2' even if we know the corresponding values of $\bar{n}$ and c_A, if 'A' is a charged ligand.

There is a further objection to use equation (6) if c_A has to be determined from p_H measurements, *whether or not the ligand is charged*. Equation (6) is a stoichiometric equation and 'x' is a stoichiometric concentration term. To evaluate 'x' we need know c_{HA} and c_A, given by the expressions:

c_{HA} = H^+ ions used up for the formation of undissociated HA

= total H^+ ions initially present (*i. e.* total acid) − H^+ ions left at equilibrium

$$= C_a - c_H{}^+ \quad \ldots \quad \ldots \quad (7)$$

$$c_A = K_a \cdot \frac{c_{HA} \cdot f_{HA}}{a_H{}^+ \cdot f_A} \quad \ldots \quad \ldots \quad (8)$$

where K_a is the thermodynamic dissociation constant of HA. From the p_H measurements, we can find the value of $a_H{}^+$ and not $c_H{}^+$. If 'A' is neutral, $f_A = 1$ but $f_{HA}{}^+$ is unknown. If, however, 'A' is a monovalent anion, $f_{HA} = 1$ since HA is neutral, but $f_A{}^-$ remains unknown. In either case, equation (8) cannot be applied to determine c_A. Bjerrum, however, has not taken these facts into consideration and has virtually put the activity coefficients equal to 1, which is not justified, even for very dilute solutions.

In the present investigation, the above method of Bjerrum has been modified to overcome the difficulties pointed out, and to make it suitable for the determination of the thermodynamic constants, 'K_1' and 'K_2', where the ligand is a charged ion. Here a new approach has been made to the problem of determining the above thermodynamic constants by noting the p_H of a set of solution mixtures, each containing in a definite volume of solution, either (*a*) a definite amount of MA_2 (in this case $PbAc_2$ or $Pb\,Prop_2$) and varying amounts of a strong acid (in this case nitric acid) or (b) a definite amount of a strong acid and varying amounts of MA_2, after the attainment of equilibrium. The activity coefficients of reacting ions have been calculated as follows.

In the following calculations we shall assume that the strong acid added is HNO_3, that the ligand is a monovalent anion A^- (the ligand involved in the present case is acetate or propionate ion) and that both HNO_3 and $M(NO_3)_2$, formed by reaction between MA_2 and HNO_3 in solution, are completely dissociated.

Now, equation (7) can be written as,

$$c_{HA} = C_a - c_H{}^+ = C_a \quad \ldots \quad \ldots \quad (7a)$$

since $c_H{}^+$ is negligible compared to C_a for our solution mixtures. Equation (8) then reduces to the form (8a).

$$a_A{}^- = \frac{K_a C_a}{a_H{}^+} \quad \ldots \quad \ldots \quad (8a)$$

since $f_{HA} = 1$, HA being neutral. An approximate value of $\bar{n}$ can be found out from equation (6) by putting $c_A{}^- = a_A{}^-$ [$a_A{}^-$ being evaluated by equation (8a) from the

experimental p_H value]. This does not entail a serious error as long as the ionic strength of the solution is low.

Equation (5) can be reduced to the form,

$$\frac{c_A^{-2}(2-\bar{n})}{\bar{n}} = k_1 \frac{c_A^{-}(\bar{n}-1)}{\bar{n}} + k_1 k_2 \quad \ldots \quad \ldots \quad (5a)$$

Putting the value of $\bar{n}$ from (6) we have

$$c_A^{-2} \cdot \frac{x}{2C-x} = k_1 c_A^{-} \cdot \frac{C-x}{2C-x} + k_1 k_2 \quad \ldots \quad (5b)$$

If we use solution mixtures of low ionic strengths, 'c_A^-' may be put equal to 'a_A^-' and 'k_1' and 'k_2' can be regarded as approximately constants. Now $c_A^{-2}.x/(2C-x)$, if plotted on the y-axis, against $c_A^{-}.(C-x)/(2C-x)$, on the x-axis, we get a nearly straight line curve, the slope of which is 'k_1' and the intercept on the y-axis is k_1k_2. The resulting plots shown in Figs. 1 and 3 are not, in fact, good straight lines, but we can draw a straight line best fitting the points in each case. As is to be expected, some of the points (for which the ionic strength is high) fall much beyond this straight line. The values of 'k_1' and 'k_2', obtained from the slope and intercept of the curves, may be regarded as approximte average values of the two above quantities over the range of low ionic strengths used.

Now, there are two alternative methods for calculating the ionic strength 'μ' and, hence, the activity coefficients of the different ions present. The first method starts from the value of 'k_2' and the second one starts from the value of 'k_1'.

Method (a).—Since any solution mixture is electrically neutral, we have

$$2c_M^{2+} + c_{MA}^{+} + c_H^{+} = c_{NO_3}^{-} + c_A^{-} \quad \ldots \quad \ldots \quad (9)$$

or,
$$2c_M^{2+} + c_{MA}^{+} \approx C_a + a_A^{-} \quad \ldots \quad \ldots \quad (9a)$$

since $c_{NO_3}^{-}$ = total nitric acid concentration C_a, c_H^{+} is negligible compared to other quantities on the left hand side of equation (9), and $c_A^{-} \approx a_A^{-}$.

Now, solving equation (4) and the electroneutrality equation (9a), we can get the approximate values of c_M^{2+} and c_{MA}^{+}, since the other quantities are known. We can now know the ionic strength 'μ' approximately from the relation (10) by inserting these values therein.

$$\mu = \tfrac{1}{2}(4c_M^{2+} + c_{MA}^{+} + c_H^{+} + c_{NO_3}^{-} + c_A^{-}) \approx \tfrac{1}{2}(4c_M^{2+} + c_{MA}^{+} + C_a + a_A^{-}) \quad \ldots \quad (10)$$

Then, since the solution mixtures used are of low ionic strengths, we can know approximate values of the activity coefficients of the ions present by application of the Debye-Hückel limiting law in the following way :

$$f_{H^+} = f_A^{-} = f_{MA^+} = f_1 = \text{antilog}\,(-0.51\sqrt{\mu}) \quad \ldots \quad \ldots \quad (11a)$$

and,

$$f_M^{2+} = f_2 = f_1^4 = \text{antilog}\,(-4 \times 0.51\sqrt{\mu}) \quad \ldots \quad \ldots \quad (11b)$$

(0.51 being the Debye-Hückel constant at the temperature of the experiment).

Method (b).—By inserting the relation (12),

$$C = c_{MA_2} + c_{MA^+} + c_M^{2+} \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

in the electro-neutrality equation (9a), we get (9b).

$$2C \approx 2c_{MA_2} + c_{MA^+} + C_a + a_{A^-} \quad \ldots \quad \ldots \quad (9b)$$

Solving (3) and (9b), we can get c_{MA_2} and c_{MA^+} and then we can get $c_M{}^{2+}$, using relation (12). Using these values of $c_{M^{2+}}$ and c_{MA^+}, we can calculate the ionic strength 'μ' from equation (10) and, hence, 'f_1' and 'f_2' by equations (11a) and (11b).

By comparing the values for the first twelve solutions (No. 1 to 12) in the case of lead acetate in Table II, it will be observed that the corresponding values of c_{MA^+} and $c_{M^{2+}}$, calculated by two independent methods (*a*) and (*b*), fairly agree with each other, differing mostly in the second significant figure. The last two values of $c_{M^{2+}}$ for solution numbers 11 and 12, calculated by method (*b*) in Table II, are, however, inaccurate because as $(c_{MA_2} + c_{MA^+})$ approaches C, the difference $c_{M^{2+}}$ (vide equation 12) would involve comparatively large error, the values of c_{MA^+} and c_{MA_2} being rather erroneous.

By comparing the corresponding values of $c_{M^{2+}}$ and c_{MA^+} for the last seventeen solutions (No. 13 to 29) in Table II, we, however, find that there is no such good agreement as in the case of the first twelve solutions. But in any case we are interested in knowing the values of $c_{M^{2+}}$ and c_{MA^+} only to calculate 'μ', 'f_1' and 'f_2'. In spite of the disagreement, mentioned above, it will be seen that both the methods, (*a*) and (*b*), yield quite concordant values of 'μ'. The values of 'f_1' and 'f_2', calculated from these values of 'μ' by equations (11a) and (11b), will therefore also be concordant. We may add that accurate values of 'c_{A^-}', recalculated from equation (8b), are practically identical in both methods (vide Table II):

$$c_{A^-} = \frac{K_a C_a}{a_{H^+} f_1} \quad \ldots \quad \ldots \quad \ldots \quad (8b)$$

The values of 'c_{A^-}', 'f_1' and 'f_2' alone are required in the subsequent calculations, and the concordance of these in the two independent methods of calculation is a sufficient guarantee for the accuracy of later evaluations.

It will be seen from Table IV, that the agreement between the corresponding values of $c_{Pb^{2+}}$ and $c_{PbProp.^+}$, calculated by the two different methods (*a*) and (*b*), is quite satisfactory in all cases, excepting in a few, where there is a little difference in the second significant figure. Nevertheless, the values of 'μ', 'f_1' and 'f_2', calculated from the data in both tables, are satisfactorily concordant, and the recalculated value of 'c_{A^-}' are almost identical.

After determining a more accurate value of 'c_{A^-}' from (8b), we can find out more accurate value of 'x' ($x = c_{A^-} + c_{HA} = c_{A^-} + C_a$). Equation (5b) is an accurate relation for every solution mixture, though 'k_1' and 'k_2' may not be constants for different solution mixtures. Inserting (1) and (2) in (5b) we have

$$c_{A^-}{}^2 \frac{x}{2C - x} \cdot f_1{}^2 f_2 = K_1 c_{A^-} \cdot \frac{C - x}{2C - x} \cdot f_2 + K_1 K_2$$

or $$Y = K_1 X + K_1 K_2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5c)$$

where, $$Y = c_{A^-}{}^2 \cdot \frac{x}{2C - x} f_1^2 f_2 \text{ and } X = c_{A^-} \cdot \frac{C - x}{2C - x} f_2.$$

The terms 'K_1' and 'K_2' in (5c) are real thermodynamic constants, and therefore the plot of 'Y' on the y-axis and 'X' on the x-axis, using the more accurate values of 'x' and 'c_{A^-}', should give a straight line curve, the slope of which gives the value of 'K_1' and the intercept of the y-axis that of "K_1K_2".

EXPERIMENTAL

Stock solutions of lead acetate (A.R.), lead propionate (prepared as given below) and nitric acid (A.R.) were prepared, in which lead was determined gravimetrically as lead sulphate and the acid by titration with a standard alkali solution. All solutions and dilutions were made with conductivity water.

Lead propionate was prepared by digesting finely powdered litharge in propionic acid (distilled and collected at 141°) on a water-bath. The resulting syrupy liquid on cooling gave a sticky white solid mass, which changed to white flakes on repeated extraction with anhydrous ether, when the excess propionic acid went in the ether layer. It was dried in vacuum and analysed. [Found: Pb (as sulphate), 59.15. Calc. for Pb $(C_2H_5COO)_2$: Pb, 58.66%].

In preparing solution mixtures in these experiments such volumes of parent stock solutions were accurately measured, which on dilution to 10 c.c. gave the desired initial molar concentration C for lead acetate or lead propionate and C_a' for nitric acid. After keeping the mixtures in a closed room for 3 hours, the p_H values were determined, using equation (13) from the E.M.F. (E) values at room temperature ($t°$) measured by a Leeds and Northrup K_2-type potentiometer. 0.1N Calomel and quinhydrone electrodes, bridged by saturated KCl solution, were used in all p_H determinations of lead acetate solution mixtures.

$$p_H = \frac{0.3625 - 0.00068\ (t - 25) - E}{0.0591 + 0.0002\ (t - 25)} \quad \ldots \quad \ldots \quad (13a)$$

Saturated calomel and quinhydrone electrodes bridged by saturated KCl solution were used in all p_H determinations of lead propionate solution mixtures.

$$p_H = \frac{0.4552 - 0.00009\ (t - 25) - E}{0.0591 + 0.0002\ (t - 25)} \quad \ldots \quad \ldots \quad (13b)$$

(Kohlthoff and Laitinen, "p_H and Electrotitration", John Wiley, 2nd ed., p. 92).

The E.M.F. reading for each solution was repeated in duplicate in all cases, and in many cases in triplicate, using each time a solution mixture independently prepared from the same stock solutions, or sometimes from different stock solutions, and in all cases the readings gave p_H values agreeing within ± 0.01 p_H units.

TABLE I

Soln. No.	C.	C_a.	$t°$.	p_H.	$a_{A^-} \times 10^3$. (Eq. 8a) ($K_a = 1.80 \times 10^{-5}$).	$*a_{A^-} - \frac{C-x}{2C-x} \times 10^3$.	$*a_{A^-}{}^{-1} \cdot \frac{x}{2C-x} \times 10^3$.
1	0.01	0.015	34.5	3.60	1.68	−1.67	0.0048
2	0.0125	,,	31.8	3.86	1.96	−1.08	0.0213
3	0.015	,,	34.5	4.06	3.10	−0.80	0.0146
4	0.020	,,	,,	4.28	5.15	−0.039	0.0269
5	0.022	,,	,,	4.36	6.19	+0.222	0.0356
6	0.025	,,	,,	4.43	7.34	+0.706	0.0430
7	0.044	,,	,,	4.68	12.92	+3.453	0.0776
8	0.066	,,	,,	4.83	18.26	+6.053	0.1123
9	0.088	,,	,,	4.92	22.47	+8.196	0.1365
10	0.110	,,	,,	4.99	26.40	+10.14	0.1615
11	0 132	,,	,,	5.02	28.28	+11.37	0.1567
12	0.154	,,	,,	5.07	31.74	+13.04	0.1803
13	0 01	0.0012	32.4	5.51	6.99	+1.071	0.0339
14	,,	0.003	31.0	5.08	6.492	+0.315	0.0385
15	,,	0.005	,,	4.80	5.68	−0.41	0.0370
16	,,	0 007	,,	4.57	4.68	−0.94	0.0307
17	,,	0.009	,,	4.37	3.80	−1.48	0.0257
18	,,	0.011	,,	4.22	3.28	−2.47	0.0269
19	,,	0.013	,,	3.98	2.23	−2.45	0.0159
20	,,	0.015	,,	3.79	1.66	−3.32	0.0137
21	0.1	0 006	,,	5.43	29.10	+11.45	0.181
22	,,	0.008	,,	5.32	30.06	+11.48	0.214
23	,,	0 010	33.2	5.19	27.87	+10.68	0.181
24	,,	0.012	,,	5.13	29.15	+10.80	0.220
25	,,	0.014	,,	5.06	28.92	+10.51	0.2285
26	,,	0.015	32.2	5.02	28.27	+10.23	0.221
27	,,	0.030	,,	4.66	24.68	+7.70	0.229
28	,,	0.045	,,	4.39	19.88	+5.17	0.190
29	,,	0.060	,,	4.19	16.72	+3.16	0.174

* 'x' has been calculated from relation $x = a_{A^-} + C_a$.

'C' and 'C_a' denote respectively the molar concentation of $PbAc_2$ and of HNO_3.

TABLE II

Solution No. (as per Table I)	Method of calculation.	$c_{M^+} \times 10^3$.	$c_{M^{2+}} \times 10^3$.	'μ'.	*$c_{A^-} \times 10^3$. (Eq. 8b)	†$Y \times 10^3$.	‡$Y \times 10^3$.
1	(a)	3.16	6.46	0.02254	1.24	−0.05674	0.00213
	(b)	3.36	6.36	0.02244	1.24	−1.018	0.00231
2	(a)	5.23	5.86	0.01281	2.27	−0.6962	0.00399
	(b)	6.19	5.39	0.02235	2.26	−0.688	0.00397
3	(a)	7.48	5.31	0.02341	3.61	−0.5556	0.00724
	(b)	8.09	5.01	0.02312	3.60	−0.5564	0.00724
4	(a)	10.87	4.64	0.02479	6.02	−0.1512	0.01321
	(b)	11.14	4.51	0 02466	6.01	−0 1530	0.01321
5	(a)	12.39	4.49	0.02559	7.26	−0 0473	0.01752
	(b)	11.77	4 71	0.02590	7.26	−0.0408	0.01736
6	(a)	13.97	4.18	0.02651	8.63	+0.2130	0.02115
	(b)	13.09	4.63	0.02697	8.64	+0.2060	0 02105
7	(a)	20.83	3 54	0.03145	15.48	+1.582	0.03654
	(b)	20.31	3.81	0.03173	15.48	+1.576	0.03621
8	(a)	26.80	3.23	0.03649	22.21	+2.750	0.05036
	(b)	26.21	3.53	0.03679	22.23	+2.740	0.05025
9	(a)	31.33	3.07	0 04054	27.66	+3.658	0.0595
	(b)	31.45	3.01	0 04048	27.65	+ 3.655	0 0592
10	(a)	35.49	2.95	0.04434	32.85	+4.413	0.0683
	(b)	35.71	2.85	0.04425	32.85	+4.416	0.0681
11	(a)	37.45	2.91	0.04618	35.38	+4.928	0.0650
	(b)	41.76	0.76	0.04404	35.17	+5.021	0.06612
12	(a)	41.05	2.84	0.04957	40.07	+5 510	0.07295
	(b)	44.97	0 89	0.04763	39.85	+5 598	0.07392
13	(a)	5.03	1.58	0.00977	7.63	+0.502	0.0229
	(b)	5.73	1.23	0.00942	7.61	+0.511	0.02301
14	(a)	5.66	1.91	0.01139	7.15	−0.0885	0.0252
14	(b)	5.29	2.10	0.01159	7.61	−0.0702	0.0247
15	(a)	6.02	2.33	0.01301	6.31	−0.536	0.0219
	(b)	5.00	2.84	0.01352	6.33	−0.562	0.02308
16	(a)	6.02	2.83	0.01451	5.24	−0.839	0.0184
	(b)	4.86	3.41	0.01509	5.24	−0.849	0.0182
17	(a)	5 93	3.43	0.01622	4.29	−1.161	0.0149
	(b)	4.56	4.12	0.01692	4.30	−1.149	0.0146
18	(a)	6.10	4.09	0.01837	3.75	−1.831	0.0154
	(b)	3.82	5.23	0.01951	3.76	−1.772	0.0149
19	(a)	5.12	5.05	0.02027	2.57	−1.674	0.00858
	(b)	3.56	5.84	0.02107	2.57	−1.634	0.00835
20	(a)	4.56	6.05	0.02271	1.03	−2.116	0.00702
	(b)	2.66	7.00	0.02366	1.94	−2.136	0.00705
21	(a)	30.48	2.31	0.03741	35.50	+5.283	0.0845
	(b)	30.48	2.31	0.03741	35.40	+5.273	0.0838
22	(a)	33.20	2.43	0.04049	37.00	+5.103	0.0963
	(b)	29.15	4.46	0.04252	37.24	+5.001	0.0948
23	(a)	32.71	2.58	0.04045	34.30	+4.772	0.0812
	(b)	31.04	3.42	0.04129	34.39	+4.731	0.0805
24	(a)	35.75	2.70	0.04385	36.30	+4.626	0.0960
	(b)	29.32	5.92	0.04707	36.46	+4.475	0.0921
25	(a)	37.25	2.83	0.04574	36.20	+4.405	0.0973
	(b)	29.18	6.87	0.04979	36.55	+4.239	0.0938
26	(a)	37.44	2.91	0.04617	35.40	+4.276	0.0929
	(b)	29.66	6.81	0.05008	35.70	+4.121	0.0894
27	(a)	46.41	4.13	0.05880	31.90	+2.817	0.0826
	(b)	30.66	12.01	0.06669	32.40	+2.632	0.0771

TABLE II (contd.)

Solution No.	Method of calculation	$c_{M^+} \times 10^3$.	$c_{M^{2+}} \times 10^3$.	'μ'	$c_{A^-} \times 10^3$.	$X \times 10^3$.	$Y \times 10^3$.
28	(a)	53.12	5.88	0.07076	26.40	+1.683	0.0593
	(b)	33.67	15.61	0.08049	26.97	+1.557	0.0553
29	(a)	60.74	7.99	0.08471	22.90	+0.852	0.0478
	(b)	34.80	20.92	0.09764	23.40	+0.767	0.0433

* $K_a = 1.75 \times 10^{-5}$ (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., p. 580).

† 'X' represents $c_{A^-} \cdot \frac{C - x}{2C - x} f_2$ and 'Y' represents $c_{A^-}{}^2 \frac{x}{2C - x} f_1^2 f_2$ where, 'f_1' and 'f_2' are calculated from the value of 'μ' by equations (11a) and (11b) and $x = c_{A^-} + C_a$.

TABLE III

Soln. No.	*C.	*C_a.	$t°$.	p_H.	$a_{A^-} \times 10^3$ (Eq. 8a) ($K_a = 1.35 \times 10^{-5}$).	$a_{A^-} \cdot \frac{C-x}{2C-x} \times 10^3$.	$a_{A^-}{}^2 \frac{x}{2C-x} \times 10^3$.
1	0.006	0.010	22.0	3.733	0.72	−2.23	0.0037
2	0.007	,,	,,	4.043	1.48	−2.49	0.0095
3	0.008	,,	,,	4.183	2.06	−2.12	0.0129
4	0.009	,,	,,	4.323	2.84	−2.11	0.0200
5	0.010	,,	22.7	4.445	3.76	−2.27	0.0312
6	0.015	,,	,,	4.712	6.96	−1.04	0.0629
7	0.020	,,	,,	4.858	9.73	+0.13	0.0921
8	0.030	,,	,,	5.05	15.15	+2.10	0.1656
9	0.040	,,	,,	5.13	18.22	+4.14	0.1810
10	0.050	,,	,,	5.22	22.39	+5.83	0.2401
11	0.055	,,	,,	5.25	24.02	+6.63	0.2583
12	0.060	,,	,,	5.27	25.14	+7.36	0.2617
13	0.065	,,	,,	5.29	26.32	+8.05	0.2685
14	0.070	,,	22.7	5.30	26.94	+8.64	0.2601
15	0.075	,,	,,	5.33	28.85	+9.38	0.2909
16	0.080	,,	,,	5.35	30.20	+10.03	0.3060
17	0.085	,,	,,	5.36	30.96	+10.56	0.3042
18	0.090	,,	,,	5.38	32.38	+11.20	0.3228
19	0.01	0.0015	22.0	5.59	7.88	+0.46	0.0548
20	0.01	0.0025	,,	5.34	7.38	+0.10	0.0530
21	0.01	0.0035	,,	5.17	6.99	−0.36	0.0538
22	,,	0.0045	,,	5.02	5.05	−0.47	0.0303
23	,,	0.0050	22.7	4.928	5.72	−0.45	0.0378
24	,,	0.010	,,	4.432	3.65	−2.10	0.0286
25	,,	0.011	21.6	4.346	3.29	−2.49	0.0272
26	,,	0.012	,,	4.193	2.53	−2.09	0.0170
27	,,	0.013	,,	4.130	2.37	−2.75	0.0186
28	,,	0.014	,,	4.022	1.98	−2.83	0.0152
29	,,	0.015	22.7	3.887	1.54	−2.77	0.0180
30	0.04	0.003	21.0	5.70	20.34	+5.97	0.1705
31	,,	0.004	,,	5.59	21.01	+6.81	0.2007
32	,,	0.005	,,	5.49	20.84	+5.45	0.2070
33	,,	0.006	,,	5.40	20.35	+5.17	0.2033
34	,,	0.007	,,	5.33	20.19	+4.89	0.2099
35	,,	0.008	,,	5.26	19.67	+4.63	0.2045

* C denotes molar conc. of $Pb(prop)_2$ and C_a, that of HNO_3.

TABLE IV

The symbols used in the table headings and their evaluations are same as in Table II.

Soln. No. (as per Table III)	Method of calculation.	$c_{M^{3+}} \times 10^3$.	$c_{M^{2+}} \times 10^3$.	'μ'	$^*c_{A^-} \times 10^3$. (Eq. 8b)	$X \times 10^3$.	$Y \times 10^3$.
1	(a)	1.05	4.83	0.01554	0.83	−1.907	0.00265
	(b)	1.20	4.76	0.01548	0.83	−1.910	0.00265
2	(a)	2.10	4.69	0.01627	1.70	−1.911	0.00590
	(b)	2.23	4.63	0.01612	1.70	−1.909	0.00559
3	(a)	2.86	4.60	0.01666	2.35	−1.527	0.00752
	(b)	3.35	4.36	0.01642	2.35	−1.533	0 00757
4	(a)	3.86	4.49	0.01733	3.26	−1.578	0.01176
	(b)	4.15	4.35	0.01719	3.26	−1.583	0.01180
5	(a)	4.99	4.38	0.01813	4.33	−1.757	0.01835
	(b)	4.73	4.52	0.01838	4.34	−1.763	0.01841
6	(a)	8.71	4.12	0.02107	8.12	−1.078	0.03617
	(b)	8.20	4.38	0.02134	8.13	−1.079	0.03608
7	(a)	11.75	3.99	0.02372	11.48	−0.445	0.05166
	(b)	11.10	4.32	0.02405	11.50	−0.449	0.05152
8	(a)	17.58	3.83	0.02902	18.24	+0.453	0.08904
	(b)	15.25	4.95	0.03010	18.30	+0.434	0.08802
9	(a)	20.71	3.75	0.03196	22.12	+1.571	0.09310
	(b)	20.35	3.94	0.03216	22.15	+1.564	0.0931
10	(a)	25.01	3.69	0.03688	27.59	+2.248	0.1202
	(b)	23.33	4.53	0.03692	27.63	+2.221	0.1189
11	(a)	26.68	3.67	0.03769	29.75	+2.594	0.1275
	(b)	25.02	4.50	0.03852	29.80	+2.566	0.1262
12	(a)	27.83	3.65	0.03778	31.22	+2.951	0.1273
	(b)	27.10	4.02	0.03916	31.24	+2.938	0.1268
13	(a)	29.03	3.64	0.03995	32.75	+3.267	0.1285
	(b)	28.99	3.67	0.03999	32.78	+3.267	0.1289
14	(a)	29.67	3.63	0.04056	33.67	+3.576	0.1244
	(b)	31.39	2.78	0.03972	33.54	+3.608	0.1247
15	(a)	31.61	3.62	0.04247	36.23	+3.814	0.1368
	(b)	32.26	3.30	0.04215	36.16	+3.829	0.1368
16	(a)	32.98	3.61	0.04381	38.00	+4.061	0.1416
	(b)	33.65	3.28	0.04348	38.00	+4.079	0.1425
17	(a)	33.76	3.60	0.04456	39.11	+4.307	0.1403
	(b)	35.60	2.68	0.04364	38.39	+4.350	0.1412
18	(a)	35.31	3.58	0.04505	41.05	+4.531	0.1472
	(b)	36.75	2.82	0.04520	40.93	+4.564	0.1478
19	(a)	5.10	2.14	0.01152	8.78	−0.152	0.0383
	(b)	6.36	1.51	0.01089	8.77	−0.149	0.0389
20	(a)	5.21	2.33	0.01220	8.29	−0.423	0.0369
	(b)	6.22	1.83	0.01171	8.26	−0.408	0.0370
21	(a)	5.39	2.55	0.01304	7.87	−0.730	0.0365
	(b)	5.97	2.26	0.01275	7.86	−0.727	0.0366
22	(a)	4.14	2.70	0.01224	7.14	−0.832	0.0325
	(b)	7.31	1.12	0.01067	7.07	−0.810	0.0331

TABLE IV (contd.)

Soln. No.	Method.	$c_{M_A}{}^+ \times 10^3$.	$c_M{}^{2+}$.	'μ'.	$^*c_A{}^- \times 10^3$.	$X \times 10^3$.	$Y \times 10^3$.
23	(a)	4.98	2.87	0.01359	6.46	−0.638	0.0246
	(b)	6.25	2.24	0.01295	6.44	−0.634	0.0280
24	(a)	4.86	4.39	0.01803	4.21	−1.628	0.0168
	(b)	4.85	4.40	0.01805	4.21	−1.628	0.0168
25	(a)	4.75	4.77	0.01906	3.81	−1.846	0.0157
	(b)	4.47	4.91	0.01920	3.81	−1.841	0.0155
26	(a)	4.02	5.25	0.01977	2.93	−1.471	0.00937
	(b)	4.50	5.02	0.01955	2.93	−1.477	0.00944
27	(a)	4.06	5.65	0.02101	2.77	−1.913	0.0103
	(b)	3.85	5.76	0.02113	2.76	−1.894	0.0101
28	(a)	3.68	6.15	0.02213	2.33	−1.998	0.00846
	(b)	3.44	6.27	0.02225	2.33	−1.994	0.00844
29	(a)	3.13	6.70	0.02323	1.83	−1.841	0.00585
	(b)	3.06	6.74	0.02328	1.83	−1.925	0.00606
30	(a)	17.62	2.86	0.02620	24.18	+2.74	0.0961
	(b)	20.80	1.27	0.02461	24.10	+2.81	0.0985
31	(a)	19.03	2.99	0.02800	25.21	+2.44	0.1124
	(b)	19.77	2.62	0.02763	25.16	+2.45	0.1225
32	(a)	19.62	3.11	0.02895	25.09	+2.24	0.1145
	(b)	19.58	3.13	0.02897	25.06	+2.24	0.1139
33	(a)	19.89	3.23	0.92958	24.55	+2.09	0.0905
	(b)	19.69	3.33	0.02968	24.54	+2.09	0.1105
34	(a)	20.49	3.35	0.03054	24.37	+1.90	0.1123
	(b)	19.47	3.86	0.03105	24.46	+1.88	0.1190
35	(a)	20.71	3.48	0.03115	23.85	+1.76	0.1084
	(b)	19.62	4.03	0.03170	23.88	+1.74	0.1078

* Using $K_a = 1.33 \times 10^{-5}$ (Harned and Owen, "Physical Chemistry of Electrolytic Solutions", 2nd ed., p. 580).

Tables I and III show for lead acetate and lead propionate solution mixtures respectively the experimentally determined p_H values of the functions

$$a_{A^-} \cdot \frac{C-x}{2C-x} \times 10^3 \qquad \text{and} \qquad a_{A^-}{}^2 \cdot \frac{x}{2C-x} \times 10^3,$$

so that equation (5b) can be represented graphically; this has been done in Fig. 1 for lead acetate solution mixtures, in which the circles represent data from Table I for the first 12 solution mixtures (No. 1 to 12) in which 'C_a' is constant and 'C' varying, and the triangles represent those for the last seventeen solution mixtures (No. 13 to 29) in which 'C' is constant and 'C_a' varying. A straight line, best fitting the majority of the points, has been drawn, and the values of 'k_1' and 'k_2' have been calculated from the slope and the intercept of this straight line, as already explained. These values are $k_1 = 13.20 \times 10^{-3}$ and $k_2 = 2.20 \times 10^{-3}$. It will be seen that some of the triangular points fall much beyond the straight line, drawn in Fig. 1. The points which spread themselves over a rather wide region in the first graph (Fig. 1), will all be observed to fall practically on a single straight line in Figs. 2A and 2B, in which data corrected from a consideration of ionic strengths have been used.

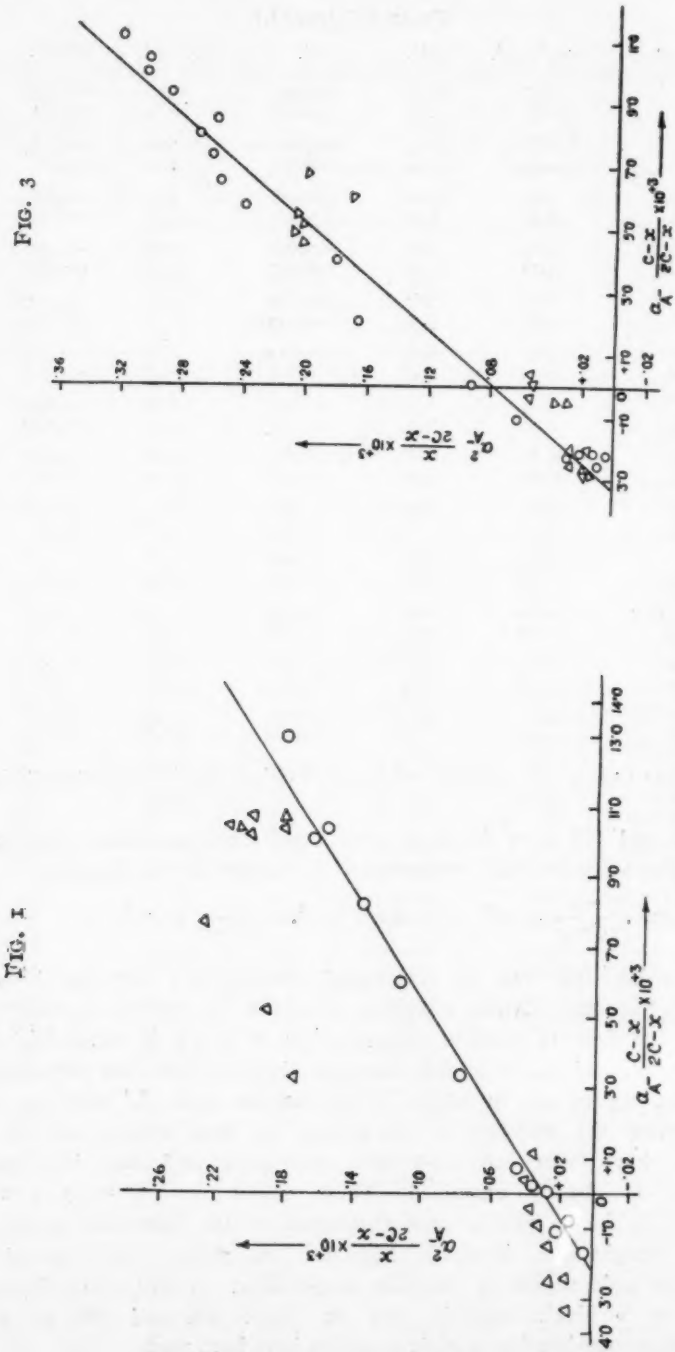


FIG. 3
FIG. 4
(Ordinate has been magnified 50 times as compared to abscissa).

Equation (5b) has been represented graphically in the case of lead propionate solution mixtures in Fig. 3, using data from Table III. Here the circles represent data for the solution mixtures from No. 1 to No. 18 (Table III) in which C_a is constant and C varying, and triangles represent those for the mixtures from No. 19 to No. 35 (Table III) where 'C' is constant and C_a varies. The slope and intercept on the ordinate of the straight line curve obtained, give the values of k_1 and k_2 as $k_1 = 23.6 \times 10^{-3}$ and $k_2 = 3.30 \times 10^{-3}$. These values may be regarded as the average values of these quantities over the range of ionic strengths employed. The first six triangular points have fallen much beyond the best fitting straight line, but it will be seen later that after making necessary corrections from a consideration of the activity coefficients of the ions, even these points come very close to the mean straight line representing equation (5c).

Table II shows the values of 'μ', 'X' and 'Y' for lead acetate solution mixtures calculated by both methods (*a*) and (*b*). 'Y' and 'X', calculated by method (*a*), have been plotted in Fig. 2A and those calculated by method (*b*) in Fig. 2B. The circles and triangles in Figs. 2A and 2B refer to solution No. 1 to 12 and 13 to 29 respectively (Table I) as in the case of Fig. 1. It will be seen that in both the plots 2A and 2B, the triangles lie in a straight line, almost parallel to another, passing through the circles, the two straight lines being very near to each other. These two straight lines should theoretically coincide, but as the values of 'μ', 'f_1' and 'f_2' used are not quite accurate, the straight lines are separated a little from each other; it must, however, be pointed out that in the graphs 2A and 2B the ordinate has been magnified one hundred times as compared to the abscissa, and this also magnifies the separation between the two straight lines. If, however, we draw a mean straight line in between the two sets of points, this will fit in both sets of data better and obviously, the slope

FIG. 2B

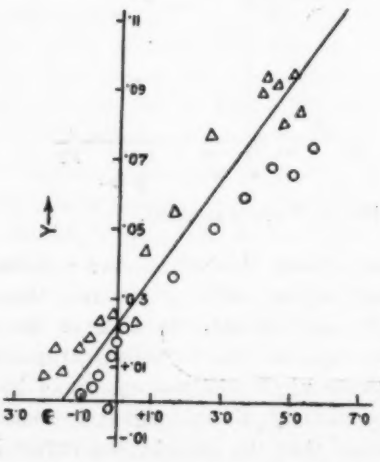
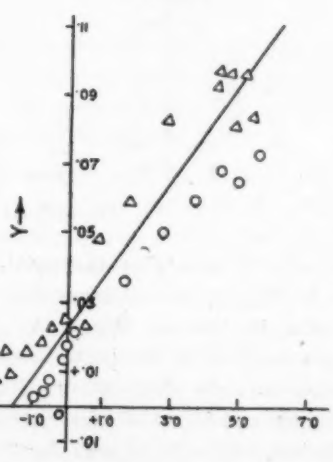


FIG. 2A



(The ordinate magnified 100 times of abscissa).

of this mean straight line more correctly represents 'K_1' and its intercept on the y-axis gives K_1K_2 more accurately than any of the two individual straight lines.

The values of 'K_1' and 'K_2', thus obtained from the mean straight line in Fig. 2A, and those obtained from the mean straight line in Fig. $2B_5$ have been found to be identical, viz., $K_1 = 14.6 \times 10^{-3}$ and $K_2 = 1.55 \times 10^{-3}$, in both cases; these are not, however, the final values (vide Discussion). The values of 'μ', 'X' and 'Y' for lead propionate solution mixtures recorded in Table IV, calculated by methods (*a*) and (*b*), are plotted in Figs. 4A and 4B respectively. The circles in the plot refer to solutions No. 1 to 18 (Table III) and the triangles to solutions No. 19 to 35 (Table III) as in Fig. 3.

FIG. 4B

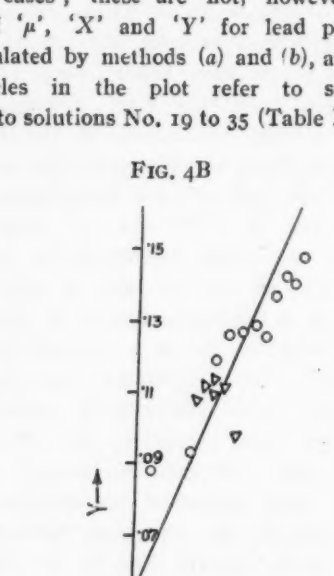
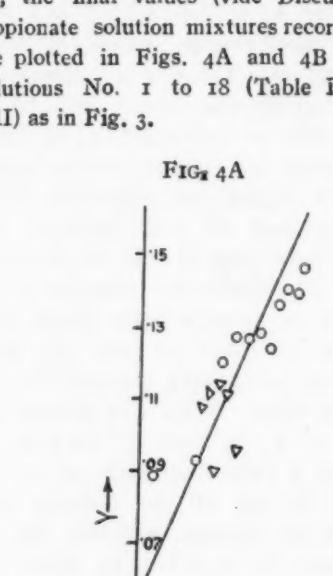


FIG. 4A



(The ordinate magnified 100 times of abscissa).

It will be seen that the points, which spread themselves over a rather wider region in Fig. 3, all condense into a very narrow strip on the two sides of the mean straight line in Figs. 4A and 4B, even though the scale of the ordinate has been doubled in the latter case. The distance of the individual points from the mean straight line in the Figs. 4A and 4B will not appear to be unduly large, if we consider that the ordinate is hundred times magnified compared to the abscissa. It will be seen by comparison that the straight line curves in Figs. 4A and 4B are identical in slope, and both cut the y-axis at the same point. So these two straight lines are identical, and evidently both the curves will give

identical values of K_1 and K_2. The values of the thermodynamic dissociation constants obtained from the graphs are $K_1 = 24.6 \times 10^{-3}$ and $K_2 = 2.20 \times 10^{-3}$. These are not, however, the final values (*vide infra*).

Discussion

The values of 'K_1' and 'K_2', obtained in the above way, however, are not independent of ionic strengths, since 'f_1' and 'f_2', calculated from the Debye-Hückel limiting law, are erroneous due to the inapplicability of the law itself in the cases of solutions with even moderately low ionic strength. The values of 'K_1' and 'K_2', obtained graphically taking data from a series of solution mixtures with different ionic strengths, as done here, can be regarded as containing a mean error corresponding to a mean ionic strength taken over the range of ionic strengths used. This can be substantiated in the following way.

The value of 'K_2', obtained here in the case of $PbAc^+$ complex, is 1.55×10^{-3} and therefore $pK_2 = 2.8097$. The mean value of 'μ', obtained from its values calculated by method (*b*) in Table II, is 0.03521 and therefore $\sqrt{\mu}_{mean} = 0.1876$. The plot of $pK_2 = 2.8097$ against $\sqrt{\mu}_{mean} = 0.1876$, is a point on the straight line curve representing $pK/\sqrt{\mu}$ plot in Part I of this paper (this *Journal*, 1958, **35**, 276; Fig. 3). In that figure the point so plotted has been shown by the mark ⊙.* If μ_{mean} is taken from the values of 'μ' calculated by method (*a*) in Table II, then also we get a nearly identical point which has not been shown in the graph.

In the case of $PbProp^+$ complex, the value of K_2 obtained here is 2.20×10^{-3}, pK_2 being therefore equal to 2.6576 and $\sqrt{\mu}_{mean} = 0.1617$, obtained from the value of 'μ' recorded in Table IV; if this value of pK_2 is plotted against the above corresponding value of $\sqrt{\mu}_{mean}$ on the $pK_2/\sqrt{\mu}_{mean}$ plot, shown in Fig. 2 in Part II of this paper (this *Journal*, 1958, **35**, 282), the point will be seen to fall on the straight line curve representing $pK_2/\sqrt{\mu}$ obtained from the data in Part II of this series (vide Fig. 2, Part II where the point under reference has been shown by ⊙ mark).*

It is quite obvious that the method of determining 'K_2' as described in Part I, is theoretically more sound and gives a more accurate value compared to the method described in Part III, since in the former method extrapolation to "$\sqrt{\mu} = 0$" is possible.

The method described in Part I for lead acetate and in Part II for lead propionate is incapable of giving the value of 'K_1', and the value of 'K_1', obtained by the method in Part III, is somewhat erroneous, as has already been indicated. A more accurate value of 'K_1' can, however be determined indirectly as follows. Though the individual values of 'K_1' and 'K_2' obtained in Part III are rather incorrect, it is expected that the ratio K_1/K_2, calculated from these values, are materially correct, as the same relative error occurs in both and comes from the same source, viz. the inapplicability of the Debye-Hückel limiting law to solutions with finite ionic strengths. Now, from this ratio K_1/K_2 and the correct value of 'K_2' from Part I, in the case of $PbAc^+$ complex and from Part II in the case of

*As the type signifying solar mark used by the authors is not available, the present sign has been used instead. Ed.

$PbProp^+$ complex, we can find an accurate value of 'K_1' in either case. The values of 'K_1', obtained in this way, and those of 'K_2', found in Parts I and II, are given below together with the values obtained by previous workers by other methods, for comparison.

TABLE V

Authors.	K_1.	K_2.	Reference.
	For $PbAc_2$.		
Present	31.2×10^{-3} at 31.0 – 34.5°	3.31×10^{-3} at 31.0 – 34.5°	"
Aditya and Prasad	30.0×10^{-3}	3.7×10^{-3}	This *Journal*, 1953, **30**, 213.
Purkayastha and Sen Sarma	...	40.76×10^{-3} at 30°	*Ibid.*, 1946, **23**, 31.
Edmond and Birnbaum	...	9.65×10^{-3} at 25° (mean value worked out from several values given)	*J. Amer. Chem. Soc.*, 1910, **62**, 2367.
Shin Suzuki	$K_1K_2 = 2.1 \times 10^{-6}$ at 25°		*J. Chem. Soc.*, Japan, Pure Chem. Sec., 1953, **74**, 531.
	For $PbProp_2$.		
Present	51.1×10^{-3} at room temp. (21-30°)	4.57×10^{-3} at room temp. (21-30°)	
Mohanty and Aditya	3.1×10^{-2} at 35°	2.2×10^{-3} at 35°	This *Journal*, 1955, **32**, 234.

The values of 'K_1' and 'K_2' for $PbAc_2$, obtained by the present authors, accord fairly well with those obtained by Aditya and Prasad by an independent and theoretically sound method. The values of 'K_2', obtained by Purkayastha and Sen Sarma and by Edmund and Birnbaum, are in our opinion erroneous for reasons already discussed in Part I of this paper. Shin Suzuki has determined the value of the constant for the equilibrium,

$$Pb^{2+} + 2HAc \rightleftharpoons PbAc_2 + 2H^+$$

to be 1.45×10^{-4} at 25°. Dividing this by K_a^2, where K_a is the ionisation constant of acetic acid, we can have the value of K_1K_2, the overall constant for the equilibrium $PbAc_2 \rightleftharpoons Pb^{2+} + 2Ac^-$, which comes out to be 2.1×10^{-6}, shown above as against our value, $K_1K_2 = 1.07 \times 10^{-4}$. Shin Suzuki, however, has overlooked the intermediate step $Pb^{2+} + HAc \rightleftharpoons PbAc^+ + H^+$ and, hence, in our opinion his value is not dependable.

Mohanty and Aditya (*loc. cit.*) have determined the thermodynamic dissociation constants K_1 and K_2 of lead propionate in aqueous solution by the measurement of solubility of lead iodate in sodium propionate solution and, also by the measurement of E.M.F. of concentration cell of the type,

$$Pb_x\ Hg_y \mid Pb(NO_3)_2 \parallel \text{Salt bridge} \parallel NaPr.Pb(NO_3)_2 \mid Pb_x\ Hg_y$$

The mean values obtained are $K_1 = 3.1 \times 10^{-2}$ and $K_2 = 2.2 \times 10^{-3}$ at 35°. These values, though of the same order as in the present work, are materially different in magnitude, being about half of those latter. A few experiments on the determination of freezing points of dilute lead propionate solutions by the present authors indicate that the values of K_1 and K_2, found in this paper, agree better with the freezing point data as compared to the values obtained by Mohanty and Aditya (*loc. cit.*). The details of the cryoscopic work will be published later.

The authors wish to express their sincere thanks to Prof. S. K. Bhattacharyya, D.Sc., F.R.I.C., F.N.I., Head of the Department of Applied Chemistry, Indian Institute of Technology, Kharagpur, for his interest and help in this work.

APPLIED CHEMISTRY DEPARTMENT,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

Received August 17, 1957.

[Jour. Indian Chem. Soc., Vol. **35**, No. 5, 1958]

SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART IV. COBALT MONO-ACETATO COMPLEX

BY S. K. SIDDHANTA AND S. N. BANERJEE

The composition of the complex formed between Co^{2+} and acetate ions has been found to be $CoAc^+$ from a study of the equilibrium H^+ ion concentrations in mixtures of equimolecular cobalt nitrate and acetic acid solutions, by "Job's method of continued variation", using a new index property, viz., the increase of H^+ ion concentration.

The thermodynamic dissociation constant, K, for the equilibrium $CoAc^+ \rightleftharpoons Co^{2+} + Ac^-$ has been found out as 30.2×10^{-3} at 29-31°, by the direct application of "law of mass action", taking into account the activity coefficients of the individual ions, calculated from the ionic strength of the mixture of cobalt nitrate and acetic acid solutions employing the "Debye-Hückel limiting law".

Thermodynamic dissociation constant, K, for the equilibrium, $(CoAc)^+ \rightleftharpoons Co^{2+} + Ac^-$

$$K = \frac{a_{Co^{2+}} \cdot a_{Ac^-}}{a_{CoAc^+}} = \frac{c_{Co^{2+}} \cdot c_{Ac^-}}{c_{CoAc^+}} \cdot \frac{f_{Co^{2+}} \cdot f_{Ac^-}}{f_{CoAc^+}}$$

has been determined by following the same procedure as adopted for lead acetato complex described in Part I of this series (this *Journal*, 1958, **35**, 269) from the determination of p_H of solution mixtures, containing a volume '$1-x$' of cobalt nitrate and 'x' of acetic acid, 'x' varying between 0.1 and 0.9, and both parent solutions being at concentration C. The composition of the complex formed has been determined as in the case of lead acetato complex (*loc. cit.*) by the application of "Job's method of continued variation", using the increase, 'Y', of

the H^+ ion concentration in the mixture, over the sum of H^+ concentrations of the parent solutions at the same dilution as the index property. From the plots of 'Y' against 'x', it has been observed that the maximum value of 'Y' corresponds to the reacting proportion 1 : 1 for cobalt nitrate and acetic acid, and this shows that under the condition of the experiment the equilibrium,

$$Co^{3+} + HAc \rightleftharpoons (CoAc)^{+} + H^{+}$$

is most prominent, and the chance of the formation of higher complexes like $CoAc_2$, $CoAc_3^-$ etc. is negligible.

Experimental

Cobalt nitrate and acetic acid used were of A.R. quality. All solutions were prepared with conductivity water. Stock solutions of cobalt nitrate and acetic acid at concentrations slightly higher than the desired value, 'C', were prepared, and in the solutions cobalt was determined gravimetrically as sulphate, and acetic acid was estimated by titration with a standard alkali solution. Then these were brought to the desired concentration 'C' by proper dilution with conductivity water. All solution mixtures shown in the tables were prepared from these parent solutions.

Fig. 1

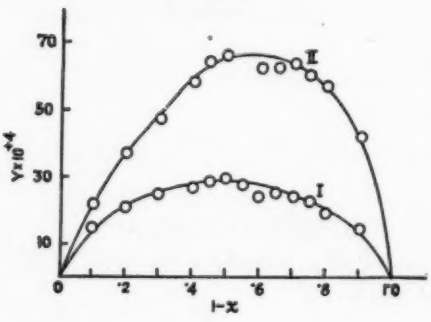


Table I

(After keeping the mixtures in a closed room for 3 hrs., the p_H values were determined by the method described in Part III, p. 323).

(HAc stands for acetic acid)

$1-x$.	Solution mixtures studied.			Conc. of parent solns. ($M/5$). $C=0.2$; $\dot{p}=1$; Temp. = 31°.		Conc. of parent solns. ($M/3$). $C=0.333$; $\dot{p}=1$; Temp. = 29°.	
	HAc.	Cobalt nitrate.	Water.	p_H.	Increase in $[H^+]$, ($Y\times10^4$).	p_H.	Increase in $[H^+]$, ($Y\times10^4$).
	9 c.c.	1 c.c.	...	2.549		2.414	
0.10	9	...	1 c.c.	2.99	14.86	2.90	21.791
	...	1	9	3.50		3.38	
	8	2	...	2.461		2.274	
0.20	8	...	2	3.00	21.04	2.92	36.723
	...	2	8	3.45		3.35	
	7	3	...	2.404		2.116	
0.30	7	...	3	3.03	24.37	2.95	47.181
	...	3	7	3.24		3.29	
	6	4	...	2.38		2.127	
0.40	6	...	4	3.06	26.81	2.97	58.032
	...	4	6	3.21		3.23	
	5.5	4.5	...	2.363		2.088	
0.45	5.5	...	4.5	3.07	28.38	2.98	64.583
	...	4.5	5.5	3.19		3.18	

TABLE I (contd.)

$1-x$.	HAc.	Cobalt nitrate.	Water.	p_H.	Conc. of parent soln.	p_H.	Conc. of parent solns.
	5	5	...	2.351		2.077	
0.50	5	...	5	3.08	29.49	2.99	66 107
	...	5	5	3.17		3.13	
	4.5	5.5	...	2.369		...	
0.55	4.5	...	5.5	3.09	27.22	...	...
	...	5.5	4.5	3.13		...	
	4	6	...	2.386		2.09	
0.60	4	...	6	3.11	24.64	3.03	62.175
	...	6	4	3.06		3.01	
	3.5	6.5	...	2.382		2.084	
0.65	3.5	...	6.5	3.12	25.00	3.06	62.980
	...	6.5	3.5	3.05		2.97	
	3	7	...	2.392		2.077	
0.70	3	...	7	3.14	23.76	3.10	64.057
	...	7	3	3.02		2.93	
	2.5	7.5	...	2.41		2.093	
0.75	2.5	...	7.5	3.18	22.29	3.12	60.544
	...	7.5	2.5	3.00		2.90	
	2	8	...	2.438		2.112	
0.80	2	...	8	3.19	19.55	3.19	57.323
	...	8	2	2.98		2.87	
	1	9	...	2.513		2.207	
0.90	1	...	9	3.28	14.22	3.23	42.072
	...	9	1	2.95		2.85	

TABLE II

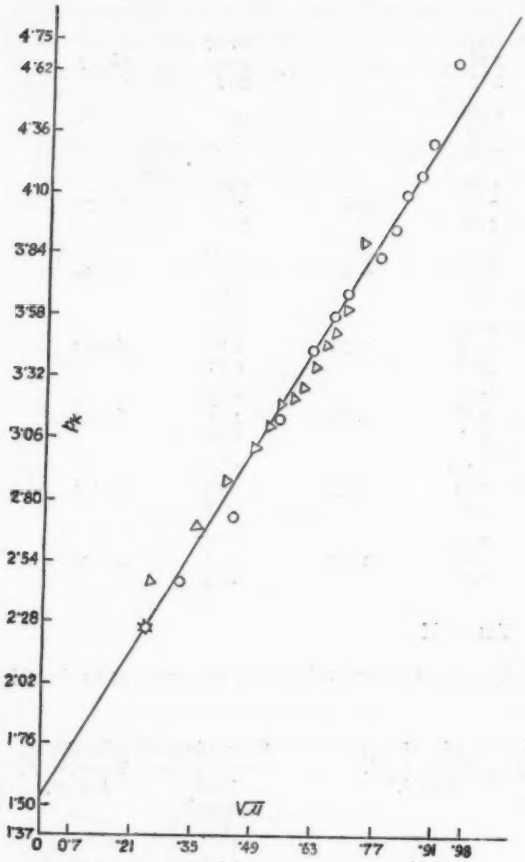
The symbols used in the table headings and their evaluations are same as in Part I (*loc. cit.*) of the series.

	Solution mixtures.		Conc. of parent soln. ($M/5$). $C=0.2$; $p=1$; Temp. $=31°$.		Conc. of parent soln. ($M/3$). $C=0.333$; $p=1$; Temp. $=29°$.	
$1-x$.	HAc. soln.	Cobalt nitrate soln.	Ionic strength (μ).	$K\times10^3$.	Ionic strength (μ).	$K\times10^3$.
0.10	9 c.c.	1 c.c.	0.0594	3.53	0.0987	3.59
0.20	8	2	0.1181	2.09	0.1962	1.39
0.30	7	3	0.1773	1.33	0.2945	0.738
0.40	6	4	0.2368	0.96	0.3930	0.382
0.45	5.5	4.5	0.2685	0.76	0.4423	0.264
0.50	5.0	5.0	0.2963	0.62	0.4918	0.209
0.55	4.5	5.5	0.3264	0.59	...	...
0.60	4.0	6.0	0.3565	0.54	0.5918	0.150
0.65	3.5	6.5	0.3864	0.44	0.6417	0.114
0.70	3.0	7.0	0.4164	0.36	0.6913	0.083
0.75	2.5	7.5	0.4465	0.31	0.7417	0.066
0.80	2.0	8.0	0.4767	0.25	0.7917	0.049
0.90	1.0	9.0	0.5371	0.13	0.8930	0.021

N.B. The ionisation constant of acetic acid (HAc) at the temperature of the experiment (29–31°) has been taken to be $K_a=1.75\times10^{-5}$ (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd. ed., p. 580).

The results of p_H measurements for mixtures of the parent solutions of cobalt nitrate and acetic acid, both at concentration $C=0.2M$ and also both at concentration $C=0.333M$, have been shown in Table I. The curves I and II in Fig. 1 represent the plots Y against x, from the data in Table I for $C=0.2M$ and that for $C=0.333M$ respectively. The values of 'μ' and 'K' for the solution mixtures have been obtained by adopting the same procedure as described in Part I of this series (*loc. cit.*), and are shown in Table II. Here also, like the case of lead acetato complex (Part I, *loc. cit.*), the plot 'K' against 'μ' from Table II yields a smooth curve, which, however, has not been used to evaluate the value of 'K' by extrapolation to zero ionic strength. The graph pK ($-\log K$) against '$\sqrt{\mu}$' represented in Fig. 2 gives a straight line curve, which on extrapolation to "$\sqrt{\mu}=0$" leads to the value of pK corresponding to the true thermodynamic constant 'K'. These values of pK and K at "$\sqrt{\mu}=0$" are 1.52 and 30.2×10^{-3} at 29-31° respectively.

FIG. 2



* Solar sign represents the plot of pK_2 against/ $\sqrt{\mu}_{mean}$ for Part V of this series (this *issue*, p. 343).

Critical review on the previous work on the subject, as also comment on the present work will be made in Part V of this series.

The authors' thanks are due to Prof. S. K. Bhattacharyya for offering facilities in carrying out this investigation.

APPLIED CHEMISTRY DEPARTMENT,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

Received August 17, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART V. COBALT ACETATO COMPLEXES

By S. K. Siddhanta and S. N. Banerjee

The p_H values of aqueous solution mixtures of cobalt acetate and nitric acid at different concentrations, after attainment of equilibrium, have been determined. The data obtained have been utilised to calculate the thermodynamic dissociation constants, K_1 and K_2, for the two successive equilibria $CoAc_2 \rightleftharpoons CoAc^+ + Ac^-$ and $CoAc^- \rightleftharpoons Co^{2+} + Ac^-$, applying a modification of Bjerrum's method described in Part III of the series. The values found at 29·31° are $K_1 = 260 \times 10^{-3}$ and $K_2 = 30.2 \times 10^{-3}$.

Cobalt acetate dissociates in aqueous solution in two stages:

$$CoAc_2 \rightleftharpoons CoAc^+ + Ac^- \quad \ldots \quad \ldots \quad (A)$$
$$CoAc^+ \rightleftharpoons Co^{2+} + Ac^- \quad \ldots \quad \ldots \quad (B)$$

The first and second thermodynamic dissociation canstants of cobalt acetate are therefore given by

$$K_1 = \frac{c_{CoAc^+} \cdot c_{Ac^-}}{c_{CoAc_2}} \cdot \frac{f_{CoAc^+} \cdot f_{Ac^-}}{f_{CoAc_2}} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

and

$$K_2 = \frac{c_{Co^{2+}} \cdot c_{Ac^-}}{c_{CoAc^+}} \cdot \frac{f_{Co^{2+}} \cdot f_{Ac^-}}{f_{CoAc^+}} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

In Part IV of this work the second dissociation constant, 'K_2', of cobalt acetate has already been determined (this *issue*, p. 339). In the present paper, by employing a modification of Bjerrum's method ("Metal Ammine Formation in Aqueous Solution", P. Haase and Sons, 1941) of determining the consecutive dissociation constants, both the first and second dissociation constants 'K_1' and 'K_2' have been found out. Essentially, in the present paper, the same procedure as adopted in Part III of this series (this *issue*, p. 323) has been followed, where theoretical details on the method have been discussed.

Experimental

Cobalt acetate pure (Johnson and Sons, Scales brand) was purified by crystallising first from acetic acid and then from absolute alcohol, when a pink coloured anhydrous salt was obtained (Ephraim and Rosenberg, *Ber.*, 1918, **51**, 134). [Found: Co (as sulphate), 32.80. Calc. for $Co(CH_3COO)_2$: Co, 33.32%].

Stock solutions of cobalt acetate and nitric acid (A.R.) were prepared and cobalt and nitric acid in them were estimated in the usual way. Such measured

volumes of stock solutions were mixed, that on dilution to 10 c.c., they produced the desired initial concentrations 'C' and 'C_a' for cobalt acetate and nitric acid respectively. After keeping the solution mixtures in a closed room for 2 hours, the p_H values were determined by following the same procedure and precautions as in Part IV (this *issue*, p. 339) of this series.

TABLE I

The symbols used in the table headings and their evaluations are same as in Part III (*loc. cit.*).

* C_a = 0.015.

Soln. No.	C*.	t°.	p_H.	$a_{A^-} \times 10^3$. ($K_a = 1.80 \times 10^{-5}$).	$a_{A^-} \times \frac{C-x}{2C-x} \times 10^3$.	$a_{A^-}{}^2 \times \frac{x}{2C-x} \times 10^3$.
1	0.012	29.7	4.205	4.30	− 6.45	0.0740
2	0.0135	,,	4.305	5.45	− 5.87	0.0937
3	0.015	,,	4.405	6.86	− 5.83	0.1272
4	0.018	29.5	4.523	9.00	− 4.50	0.1619
5	0.020	30.6	4.587	10.43	− 3.86	0.1892
6	0.021	29.5	4.615	11.13	− 3.57	0.2033
7	0.024	,,	4.681	12.95	− 2.59	0.2348
8	0.030	30.6	4.838	18.60	− 2.54	0.4402
9	0.040	,,	4.953	24.24	+ 0.475	0.5644
10	0.050	,,	5.040	29.61	+ 2.89	0.7057
11	0.065	29.8	5.12	35.58	+ 6.45	0.8069
12	0.078	,,	5.10	40.85	+ 9.02	0.9317
13	0.0845	,,	5.20	42.80	+10.28	0.9519
14	0.091	,,	5.22	44.78	+11.44	0.9813
15	0.0975	,,	5.24	46.96	+12.53	1.028
16	0.104	,,	5.26	49.09	+13.61	1.074
17	0.117	,,	5.29	52.64	+15.66	1.126
18	0.120	29.7	5.30	53.91	+16.10	1.170
19	0.140	,,	5.35	60.40	+19.06	1.345
20	0.160	,,	5.37	63.24	+21.40	1.293
21	0.170	,,	5.38	64.76	+22.45	1.286
22	0.180	,,]	5.39	66.34	+23.50	1.284

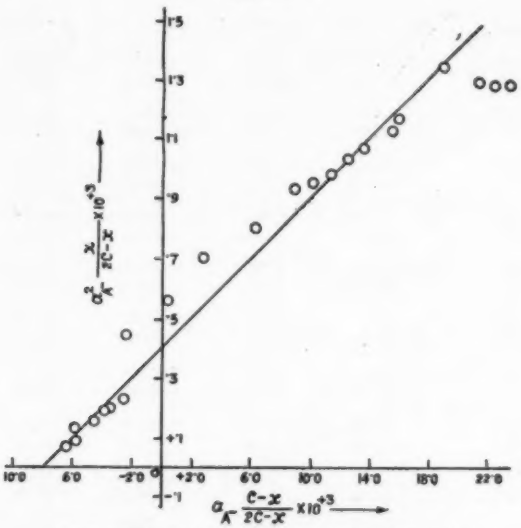
* C and C_a denote respectively molar concentration of $CoAc_2$ and HNO_3.

Table I shows the experimental p_H values and the corresponding values of the functions

$$a_{A^-} \cdot \frac{C-x}{2C-x} \times 10^3 \quad \text{and} \quad a_{A^-}{}^2 \cdot \frac{x}{2C-x} \times 10^3$$

(where A^- stands for acetate ion and 'x', total concentration of "free acetic acid species" given by $c_{A^-} + C_a$). Fig. 1 represents equation (5b) (vide Part III, *loc.*

FIG. 1



(Ordinate magnified 20 times that of abscissa).

c.t.) graphically. (For solutions of low ionic strengths 'c_A-' may be put equal to 'a_A-' in equation 5b). The slope and intercept on the ordinate, of the straight line curve obtained, give the values of k_1 and k_2 as respectively 50.0×10^{-3} and 8.00×10^{-3}. These may be regarded as the average values of k_1 and k_2 over the range of ionic strengths employed.

TABLE II

The symbols used in the table headings and their evaluations are same as in Part III (*loc. cit.*).

Soln. No (same as in Table I.)	Method of calculation.	$c_{M^{A+}} \times 10^3$.	$c_{M^{2+}} \times 10^3$.	μ.	$c_A^- \times 10^3$ (using $K_a = 1.75 \times 10^{-5}$).	$X \times 10^3$.	$Y \times 10^3$.
1	(*a*)	4.09	7.60	0.02689	5.10	−4.902	0.0422
	(*b*)	4.01	7.65	0.02695	5.10	−4.897	0.0421
2	(*a*)	5.18	7.61	0.02803	6.42	−4.075	0.0480
	(*b*)	5.37	7.54	0.02799	6.45	−4.210	0.0494
3	(*a*)	6.56	7.65	0.02951	8.16	−4.343	0.0672
	(*b*)	6.38	7.74	0.02960	8.16	−4.339	0.0671
4	(*a*)	8.64	7.68	0.03168	10.78	−3.556	0.0836
	(*b*)	8.82	7.59	0.03159	10.78	−3.559	0.0837
5	(*a*)	10.02	7.69	0.03310	12.56	−3.226	0.0966
	(*b*)	10.28	7.58	0.03301	12.55	−3.241	0.0968
6	(*a*)	10.72	7.70	0.03382	13.42	−3.091	0.1032
	(*b*)	10.98	7.58	0.03371	13.42	−3.059	0.1033
7	(*a*)	12.50	7.72	0.03566	15.73	−2.523.	0.1163
	(*b*)	13.30	7.28	0.03513	15.69	−2.514	0.1165
8	(*a*)	18.05	7.77	0.04136	22.95	−3.174	0.216
	(*b*)	15.13	9.24	0.04284	23.05	−3.196	0.214
9	(*a*)	23.63	7.80	0.04703	30.40	−1.709	0.2629
	(*b*)	20.69	9.28	0.04852	30.51	−1.732	0.2603

TABLE II (contd.)

Soln.	Method.	$c_{MA}^{+} \times 10^3$.	$c_{M^+}^{+} \times 10^3$.	μ.	$c_{A^-} \times 10^3$.	$X \times 10^1$.	$Y \times 10^3$
10	(a)	28.95	7.82	0.05242	37.66	−0.719	0.314
	(b)	25.35	9.63	0.05424	37.83	−0.758	0.310
11	(a)	34.89	7.84	0.05841	45.97	+0.862	0.3398
	(b)	32.77	8.91	0.05949	45.05	+0.838	0.3367
12	(a)	40.14	7.85	0.06369	53.40	+1.787	0.3760
	(b)	38.02	8.92	0.06477	53.54	+1.752	0.3738
13	(a)	42.07	7.86	0.06565	56.21	+2.293	0.3783
	(b)	41.00	8.40	0.06620	56.27	+2.274	0.3767
14	(a)	44.04	7.87	0.06765	59.12	+2.726	0.3841
	(b)	43.78	8.00	0.06779	59.10	+2.724	0.3829
15	(a)	46.21	7.87	0.06982	62.20	+3.098	0.3941
	(b)	46.22	7.87	0.06983	62.27	+3.091	0.3951
16	(a)	48.34	7.87	0.07195	65.39	+3.434	0.407
	(b)	48.55	7.77	0.07186	65.37	+3.436	0.407
17	(a)	51.87	7.88	0.07551	70.75	+4.102	0.4176
	(b)	53.56	7.04	0.07468	70.52	+4.144	0.4180
18	(a)	53.13	7.89	0.07680	72.51	+4.202	0.4282
	(b)	54.02	7.86	0.07627	72.45	+4.226	0.4301
19	(a)	59.61	7.89	0.08328	82.41	+4.956	0.4742
	(b)	59.89	7.76	0.08316	82.39	+4.960	0.4744
20	(a)	62.44	7.90	0.08614	86.80	+5.830	0.444
	(b)	68.49	4.92	0.08320	86.25	+5.976	0.4512
21	(a)	63.95	7.90	0.08765	88.98	+6.195	0.4331
	(b)	72.48	3.64	0.08340	88.36	+6.407	0.4456
22	(a)	65.54	7.96	0.08924	91.58	+6.518	0.4298
	(b)	76.26	2.54	0.08388	90.62	+6.796	0.4429

The values of 'μ', 'X' and 'Y', calculated by the two independent methods (*a*) and (*b*), described in Part III of this series (*loc. cit.*), have been shown in Table II. The values of 'Y' and 'X' from Table II, calculated by methods (*a*) and (*b*), are plotted in Figs. 2A and 2B respectively. It will be found on examination that both the two straight lines in Figs. 2A and 2B are identical in respect of slope and intercept on the ordinate, and hence, the values of 'K_1' and 'K_2' obtained from both are identical and are respectively 47.3×10^{-3} and 5.50×10^{-3}. These are not, however, the final values (vide Discussion).

DISCUSSION

As explained in Part III (*loc. cit.*), the values of 'K_1' and 'K_2' obtained in the present paper are graphically taken mean values containing a mean error corresponding to the mean ionic strength for the solutions studied. This point can be substantiated, in the present case too, by ploting $pK_2 = (-\log K_2) = 2.2596$ found from the value of $K_2 = 5.50 \times 10^{-3}$ obtained above, against $\sqrt{\mu}_{\text{mean}} = 0.2388$, calculated from the values of 'μ' in Table II, on the $pK/\sqrt{\mu}$ plot shown in Fig. 2, Part IV (*loc. cit.*). The point representing $pK/\sqrt{\mu}_{\text{mean}}$ in the present case (shown by solar sign mark in Fig. 2, Part IV) will be seen to fall on the straight line curve representing $pK_2/\sqrt{\mu}$ obtained from the data in Part IV.

FIG. 2A

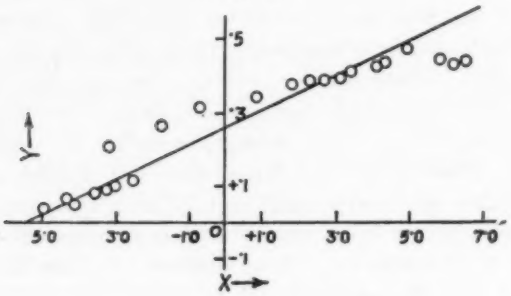
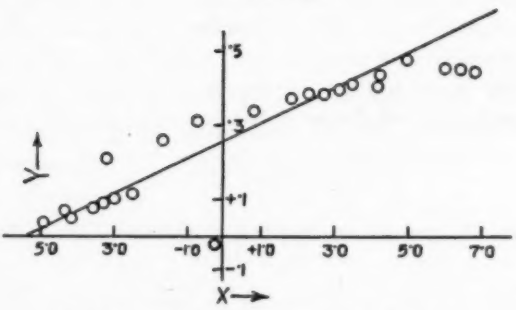


FIG. 2B



(Ordinate magnified 10 times that of abscissa).

As has already been explained in Part III, the ratio K_1/K_2, obtained in this communication, may be taken to be correct, while the value of 'K_2' determined in Part IV (*loc. cit.*) is essentially correct; therefore a correct value of 'K_1' can now be calculated out. The correct values are therefore $K_1 = 260.0 \times 10^{-3}$ and $K_2 = 30.2 \times 10^{-3}$ at 29-31°.

The only previous work on this subject appears to be that of Bardhan and Aditya (this *Journal*, 1955, **32**, 109) who from a measurement of the E.M.F of the cell conclude that the first stage dissociation of cobalt acetate in aqueous solution represented by equation (A) is virtually complete, and the thermodynamic constant for the equilibrium (B) representing the second stage dissociation is given by $K_2 = 43.5 \times 10^{-3}$ at 35°. In our opinion, the conclusion of the above authors about the first stage of dissociation being complete, is rather an assumption than a definite conclusion. The authors calculated the value of the degree of dissociation 'β' for the second stage, assuming that the first stage dissociation was complete. Since the value of 'β', thus calculated from the E.M.F. data, ranged from 0.95 to 0.60 for different dilutions of cobalt nitrate and sodium acetate solutions, they argued, "the values of 'β' show that complete dissociation of the first stage is justified." Had the first stage of dissociation been considered at the very outset, the values of 'β' would have been otherwise in our opinion.

On the other hand, we can establish definitely from the data obtained in the present work that the first step dissociation for cobalt acetate is substantially incomplete by the following considerations. If the first step dissociation is complete, the value of 'x' (free acetate species : $c_{Ac^-} + c_{HAc}$) for any solution mixtures of cobalt acetate (conc. C) and nitric acid (conc. C_a) should be always much greater than 'C'. The maximum ionic strength possible for such solution mixtures is equal to "$3C$", which is attained when even the second stage dissociation is complete*. The value of activity coefficient 'f_1' of acetate ion, calculated from this maximum possible value of 'μ', would be the minimum possible value of 'f_1' for the solution mixture. If we calculate c_{Ac^-} from equation (8b) (Part III, *loc. cit.*), using this minimum value of 'f_1', that value would be maximum possible for c_{Ac^-}, and the value of 'x', calculated from this c_{Ac^-}, would also be maximum possible. It will be seen from Table III that for some of the solution mixtures (viz. No. 15 to 22), the value of x/c, thus calculated, hardly exceeds one. If the complete first step dissociation preceded any pronounced second step dissociation, the value of 'x' could not have been so low, particularly in view of the fact that there is additional decomposition of $CoAc^+$ species in presence of the nitric acid.

TABLE III

[The values of x considering the first step dissociation to be complete].

Soln. No. (as per Table I)	$\mu = 3C$.	f_1.	$c_{Ac^-} = \frac{K_a C_a}{a_{H^+} f_1}$.	$x = c_{Ac^-} + C_a$.	x/c.
15	0.2925	0.5299	0.0861	0.1011	1.03
16	0.312	0.5189	0.0920	0.1070	1.02
17	0.351	0.4956	0.1026	0.1176	1.005
18	0.360	0.4943	0.1060	0.1210	1.008
19	0.420	0.4672	0.1256	0.1406	1.004
20	0.480	0.4433	0.1386	0.1536	0.96
21	0.510	0.4323	0.1456	0.1606	0.94
22	0.540	0.4220	0.1528	0.1678	0.93

It may therefore be concluded that the results obtained in the present work are more reliable than those of Bardhan and Aditya (*loc. cit.*) who start with an *ad hoc* assumption which is observed to be against experimental facts.

Thanks of the authors are due to Professor S. K. Bhattacharyya for offering facilities.

APPLIED CHEMISTRY DEPARTMENT,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

Received August 17, 1957.

* $\mu = \frac{1}{2}[4\,c_{Co^{++}} + (2c_{Ac^-} - c_{HAc}) + c_{H^+} + c_{NO_3^-}] = \frac{1}{2}[4C + 2C - C_a + C_a] = 3C$ assuming complete dissociation for cobalt acetate into cobalt and acetate ions and knowing the facts that $c_{NO_3} = C_{a^+} = c_{HAc}$ and c_{H^+} is negligible.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART VI. MANGANESE MONO-ACETATO COMPLEX

By S. K. Siddhanta and S. N. Banerjee

The composition of the complex formed between Mn^{2+} and acetate ions has been found to be $(MnAc)^+$, from a study of the equilibrium H^+-ion concentrations in mixtures of equimolar manganese chloride and acetic acid solutions, by "Job's method of continued variation", using a new index property, viz., the increase of hydrogen-ion concentration.

The thermodynamic dissociation constant, K, for the equilibrium, $MnAc^+ \rightleftharpoons Mn^{2+} + Ac^-$, has been found to $6c.3 \times 10^{-2}$ at $28.3 - 30.0°$, by the direct application of "law of mass action", taking into account the activity coefficients of individual ions, calculated from the ionic strength of the solution mixture of manganese chloride and acetic acid solutions, employing the "Debye-Hückel limiting law".

The procedure described in Part I (this *Journal*, 1958, **35**, 269) of this series for lead acetato complex was applied here for the determination of the thermodynamic dissociation constant 'K' for the equilibrium, $(MnAc)^+ \rightleftharpoons Mn^{2+} + Ac^-$ (where Ac^- represents acetate ion).

$$K = \frac{a_{Mn^{2+}} + a_{Ac^-}}{a_{MnAc^+}} = \frac{c_{Mn^{2+}}\ c_{Ac^-}}{c_{MnAc^-}} \cdot \frac{f_{Mn^{2+}}\ f_{Ac^-}}{f_{MnAc^+}}$$

In the present case the p_H values for solution mixtures, containing a volume '$1\text{-}x$' of manganese chloride and 'x' of acetic acid, 'x' varying between 0.1 and 0.9 with both parent solutions at concentration, 'C', were determined. The composition of the complex formed has been found out, as in the case of lead acetato complex (*loc. cit.*) by the application of "Job's method of continued variation" using the increase (Y) of the hydrogen-ion concentration in the mixture over the total hydrogen-ion concentrations of the parent solutions at the same dilution, as the index property. From the Y/x plots it has been observed that the maximum value of 'Y' corresponds to the reacting proportion 1 : 1 for manganese chloride and acetic acid. This shows that under the present experimental conditions, the following equlibrium alone is most predominant, and the formation of higher complexes, e.g. $MnAc_2$, $MnAc_3^-$ etc., is negligible. The reaction can therefore be written as, $Mn^{2+} + HAC \rightleftharpoons (MnAc)^+ + Ac^-$, assuming complete dissociation of manganese chloride and hydrochloric acid.

Experimental

Manganese chloride and acetic acid used were of Analar variety. All solutions of manganese chloride and acetic acid were prepared in conductivity water and in stock solutions manganese was determined as sulphate, and the acid by titration with a standard alkali solution. These were used to prepare solutions of desired concentration 'C'. After keeping the mixtures, as shown in Table I, in a closed room for 3 hours, the p_H values were determined by following an identical procedure and observing same precautions as adopted in Part II (this *Journal*, 1958, **35**, 279).

TABLE I

[HAc stands for acetic acid]

1-x.		Solution mixtures studied. Concentrations of parent solutions. $M/5$; $C = 0.2$; Temp = 30°; $M/2$; $C = 0.5$; $p = 1$; $p = 1$; Increase in $[H^+]$			Temp. = 28.3°; Increase in $[H^+]$.			
		HAc.	$MnCl_2$.	Water.	p_H.	$(Y \times 10^4)$.	p_H.	$(Y \times 10^4)$
	(i)	9 c.c.	1 c.c.	...	2.727		2.453	
0.1	(ii)	9	...	1 c.c	2.764	1.35	2.73	16.62
	(iii)	...	1	9	4.74		...	
	(i)	8	2	...	2.702		2.418	
0.2	(ii)	8	...	2	2.790	3.54	2.75	20.41
	(iii)	...	2	8	4.98		...	
	(i)	7	3	...	2.699		2.401	
0.3	(ii)	7	...	3	2.819	4.75	2.775	22.93
	(iii)	...	3	7	5.11		...	
	(i)	6	4	...	2.709		2.395	
0.4	(ii)	6	...	4	2.857	5.57	2.80	24.42
	(iii)	...	4	6	5.15		...	
	(i)	5	5	...	2.727		2.401	
0.5	(ii)	5	...	5	2.895	5.91	2.837	25.17
	(ii)	...	5	5	5.13		...	
	(i)	4	6	...	2.757		2.421	
0.6	(ii)	4	...	6	2.947	6.13	2.88	24.75
	(iii)	...	6	4	5.13		...	
	(i)	3	7	...	2.805		2.451	
0.7	(ii)	3	...	7	3.01	5.83	2.926	23.54
	(iii)	...	7	3	5.14		...	
	(i)	2	8	...	2.877		2.508	
0.8	(ii)	2	...	8	3.09	5.07	2.996	20.93
	(iii)	...	8	2	5.15		...	
	(i)	1	9	...	3.01		2.623	
0.9	(ii)	1	...	9	3.27	4.33	3.10	15.39
	(iii)	...	9	1	5.16		...	

* It is found from experiments with $C = 0.2$, that amount of H^+ ions liberated, when manganese chloride is dissolved in water, is negligible as compared to those in solutions (i) and (ii) and also to the value of Y. Therefore at $C = 0.5$, it is neglected.

TABLE II

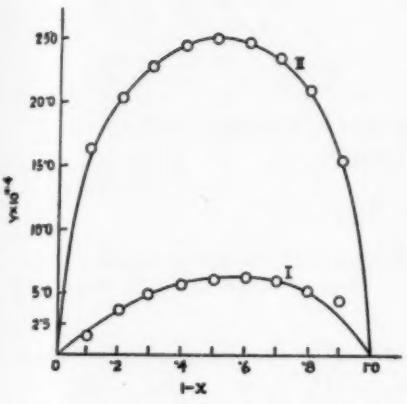
The symbol used in the table headings and their evaluations are same as in Part I (*loc. cit.*).

1-x.	Solution mixtures. HAc.	$MnCl_2$.	Conc. of parent solutions ($M/5$). $C = 0.2$, $p = 1$; Temp. = 30°. μ.	$K \times 10^3$.	Conc. of parent soln. ($M/2$). $C = 0.5$; $p = 1$; Temp. = 28.3°. μ.	$K \times 10^3$.
0.1	9	1	0.0614	46.69	0.1509	12.95
0.2	8	2	0.1208	17.54	0.2998	6.54
0.3	7	3	0.1804	11.86	0.4498	3.76
0.4	6	4	0.2402	8.98	0.5985	2.32
0.5	5	5	0.2999	6.91	0.7482	1.50
0.6	4	6	0.3598	5.47	0.8980	1.01
0.7	3	7	0.4197	4.45	1.048	0.67*
0.8	2	8	0.4797	3.55	1.198	0.44*
0.9	1	9	0.5397	2.71	1.348	0.28*

* These could not be shown in Fig. 2.

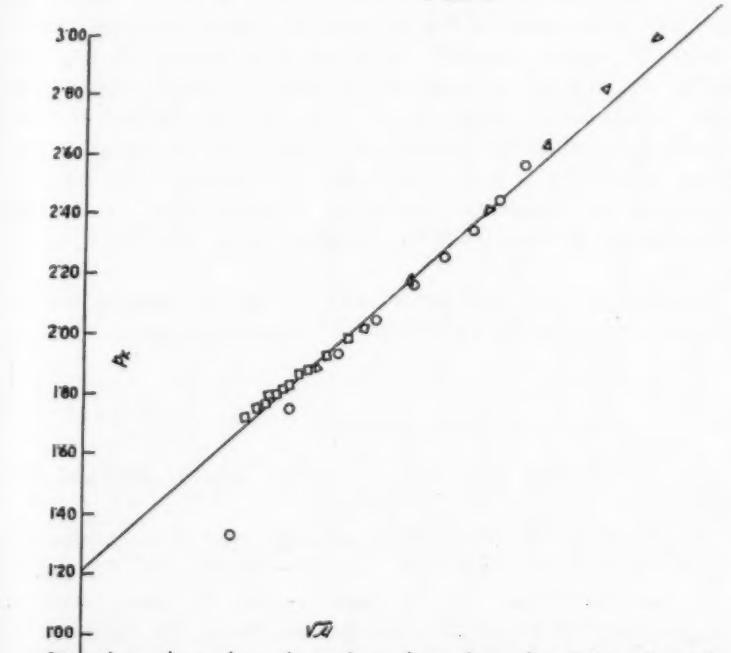
N. B. Ionisation const. of HAC at 28.3-30° was taken to be $K_a = 1.75 \times 10^{-5}$ (Hurned and Owen, *loc. cit.*).

FIG. 1



The results of p_H measurements for mixtures of the parent solutions of manganese chloride and acetic acid, both at concentration $C = 0.2\ M$ and also both at $C = 0.5\ M$, have been shown in Table I. The curves I and II in Fig. 1 represent the Y/x plots from the data in Table I for $C = 0.2\ M$ and that for $C = 0.5M$ respectively. The values of 'μ' and 'K' for the solution mixtures have been obtained by following the same procedure as discussed in Part I (*loc. cit.*) and are shown in Table II. As in Part I, here also K/μ plot from the data in Table II gives a smooth curve showing the dependence of 'K' on the corresponding ionic strength 'μ', the reason being the inapplicability of the "Debye-Hückel limiting law' to solutions of finite ionic strengths. This curve, however, has not been used to determine the value of 'K' by extrapolation to zero ionic strength. The plot $pK(= -\log K)$ against '$\sqrt{\mu}$' gives a straight line curve as represented in Fig. 2, which when extrapolated to '$\sqrt{\mu} = 0$' gives the value of pK corresponding to the thermodynamic constant 'K'. These values of pK and 'K' at "$\sqrt{\mu} = 0$" are 1.22 and 60.3×10^{-3} at 28.3 – 30° respectively.

FIG. 2



The authors' best thanks are due to Prof. S. K. Bhattacharyya for offering facilities.

APPLIED CHEMISTRY DEPARTMENT,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

Received August 17, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

COMPOUNDS OF NICKEL IODIDE WITH AMINES AND HETEROCYCLIC BASES

By Sarju Prasad and V. Krishnan

Several compounds of nickel iodide with amines have been prepared by the action of primary (mono and di), secondary and tertiary amines and heterocyclic bases on nickel iodide in ether, their properties studied and their structures discussed.

Nickel usually exhibits a co-ordination number of six, but compounds in which it is four are also reported in literature. Erdmann (*J. prakt. Chem.*, 1866, **97**, 395) and Laurent (*Ann. chim. phys.*, 1852, **36**, 353) obtained $[Ni(NH_3)_4](NO_3)_2$, $2H_2O$ by the action of ammonia on $Ni(NO_3)_2$. Ephraim and Moser (*Ber.*, 1920, **53**, 548) prepared $[Ni(NH_3)_6]A_2$ and $[Ni(NH_3)_4]B_2$ and showed that the formation of ammines with more than six ammonia groups in salts of small cation and large organic anion was independent of the presence of organic residues. Spacu (*Chem. Zentrl.*, 1924, II, 2650) obtained $[Ni(C_{12}H_{12}N_2)_2].(H_2O)_2$. $(NO_3)_2$ and $[Ni(C_{12}H_{12}N_2)_2].(H_2O)_2$ by mixing an alcoholic solution of nickel nitrate with benzidine in alcohol. Rammelsberg (*Pogg. Ann.*, 1839, **48**, 119) claimed to have prepared tetrammino-nickel iodide by the action of ammonia on nickel iodide. Blitz and Fetkenheuer (*Z. anorg. Chem.*, 1913, **83**, 163) obtained $[Ni(NH_3)_2]I_2$ by thermal decomposition of hexammino derivative. Ephraim (*Ber.*, 1921, **54B**, 379) prepared $[Ni(NH_3)_4]I_2$ to $6I_2$, $[Ni(NH_3)_4]I_2.HgI_2$. $4H_2O$ and $[Ni(NH_3)_4]I_2$-HgI_2, $2H_2O$.

The present investigation was undertaken with a view to studying the formation of the compounds of nickel iodide with amines and heterocyclic bases.

Experimental

The amines and nickel iodide used were of B.D.H. pure quality, and ether was distilled over sodium.

General Method of Preparation.—A dilute ethereal solution of amine was added to nickel iodide solution in ether with constant shaking till the precipitation was complete and the amine was in slight excess. In some cases, the precipitate was obtained only at a low temperature and, hence, the mixture was kept in a refrigerator. It was filtered, washed with anhydrous ether till the washings did not give any precipitate with nickel iodide. It was dried at the room temperature, analysed and its properties studied.

Iodine was estimated as silver iodide and nickel as dimethylglyoxime complex. The organic matter was found by difference.

TABLE I

†Compounds formed

Amine

8—1

TABLE 1

Amine	‡Compounds formed.	Colour.	M.P.	% Nitrogen Found.	% Nitrogen Calc.	% Iodine. Found.	% Iodine. Calc.	% Organic substance. Found.	% Organic substance. Calc.
α-Naphthylamine	4-α-A.NiI_2 $[Ni(C_{10}H_7NH_2)_4]I_2$	Dark green	101°	5.20	5.27	28.60	28.69	66.20	66.04
β-Naphthylamine	4-β-A. NiI_2 $[Ni(C_{10}H_7NH_2)_4]I_2$	Do	20°	5.16	5.27	28.52	28.69	66.32	66.04
p-Toluidine	4-A. NiI_2 $[Ni(C_6H_4CH_3.NH_2)_4]I_2$	Bluish grey	22°	7.80	7.93	33.98	34.28	58.22	57.709
Benzylamine	4-A. NiI_2* $[Ni(C_6H_5CH_2NH_2)_4]I_2$	Bluish pink		7.86	7.93	33.82	34.28	58.32	57.79
	Diamines.								
Benzidine	2-A. NiI_2 $[NiC_{12}H_8(NH_2)_2]I_2$	Dark blue	102°	11.71	11.82	50.89	51.12	38.40	37.06
o-Dianisidine	2-A. NiI_2 $[Ni\{CH_3O(NH_2)C_6H_3.C_6H_3NH_2OCH_3\}_2]I_2$	Bluish green	164°	10.40	10.51	44.86	45.44	44.74	44.05
o-Phenylenediamine	2-A. NiI_2 $[Ni\{C_6H_4(NH_2)_2\}_2]I_2$	Dark blue	168°**	10.89	11.11	47.96	48.03	41.15	40.86
p- ,,	2-A. NiI_2 $[Ni\{C_6H_4(NH_2)_2\}_2]I_2$	Do	260°	10.96	11.11	47.94	48.03	41.10	40.86
o-Tolidine	2-A. NiI_2 $[Ni(CH_3NH_2.C_6H_3.C_6H_3.NH_2CH_3)_2]I_2$	Bluish grey	240°	7.86	7.97	33.92	34.45	58.22	57.581
Phenylhydrazine	2-A. NiI_2 $[Ni(C_6H_5NH\ NH_2)_2]I_2$	Yellow	18°	10.80	11.11	47.89	48.03	41.31	40.86
	Secondary amines.								
Diphenylamine	4-A. NiI_2 $[Ni\{(C_6H_5)_2NH\}_4]I_2$	Light green	158°	5.87	5.94	24.98	25.61	69.15	68.46
Dibenzylamine	4-A. NiI_2* $[Ni\{(C_6H_5CH_2)_2NH\}_4]I_2$	Bluish green		5.02	5.33	22.89	23.07	72.09	71.59
	Tertiary amines.								
Triethylamine	1-A. NiI_2 $[Ni(C_2H_5)_3N]I_2$	Yellow	174°	14.06	13.82	62.08	61.76	23.86	44.42
Triethylamine	4-A. NiI_2 $[Ni\{(C_2H_5)_3N\}_4]I_2$	Do	179°	7.85	8.00	35.92	35.50	56.23	56.44
Diethylaniline	4-A. NiI_2* $\left[Ni\left\{\begin{matrix}(C_2H_5)_2\\(C_6H_5)\end{matrix}\right\rangle N\right\}_4\Big]I_2$	Dark blue		6.29	6.32	28.20	28.26	65.51	65.42
	Heterocyclic bases.								
Piperazine	4-A. NiI_2 $[Ni(C_4H_8N_2H_2)_4]I_2$	Bluish green	210°**	8.84	8.94	38.69	38.67	52.57	52.39
Piperidine	4-A. NiI_2 $[Ni(C_5H_{10}NH)_4]I_2$	Greenish yellow	139°	8.90	9.00	19.42	19.44	71.68	71.55

* Liquid compounds. ‡ A stands for corresp. amine. ** Decomposed at its melting point.

Properties.—The co-ordination number of nickel in all the cases studied is four. In the case of triethylamine, however, a precipitate is formed with one molecule of the amine which dissolves on further addition of the amine solution and is reprecipitated. The compounds are stable in dry atmosphere but decompose when treated with strong acids. They are sparingly soluble or insoluble and fairly stable in cold water but decompose slowly on boiling. On heating alone, they decompose and iodine is liberated.

It appears that the amines and heterocyclic bases attach themselves to the central atom, chelate compounds being formed in the case of diamines and can be represented as $[Ni(4A)]I_2$ where A is a primary, secondary or tertiary amine or a heterocyclic base and $[Ni(2D)]I_2$ where D is a diamine. In the case of secondary and tertiary amines, the reaction is similar to that with the primary amines with the difference that the precipitate appears only on shaking the mixture for a long time at the room temperature, showing thereby the weak co-ordination power of : NH and : N groups.

Thanks are due to Dr. S. S. Joshi, D.Sc., Head of the Department of Chemistry, Banaras Hindu University, for providing necessary facilities.

CHEMISTRY DEPARTMENT,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

Received January 10, 1958.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

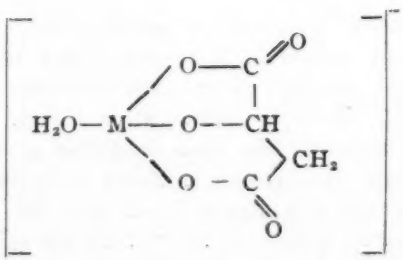
MALATE COMPLEX OF COPPER

By Ch. B. Nanda and S. Pani

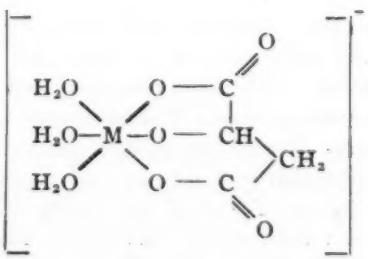
Malate complex of copper has been investigated by p_H titration method within the p_H range of 2 to 6. A neutral complex A_1 is formed at lower p_H due to the reaction of a copper ion and malic acid with the liberation of the two protons. The equilibrium constant of the reaction has been found to be 3.89×10^{-5}. This complex with increase in p_H dissociates into a H^+ ion and complex C_1^-, the dissociation constant being 4.74×10^{-5}.

Malate complex of copper was studied by Delsal (*J. chim. phys.*, 1938, **35**, 314) and the existence of a complex was postulated from two sets of polarimetric measurements and by electrometric measurements.

Many metals form 1 : 1 complex with tartrate and citrate ligands. Similar 1 : 1 complexes are also expected with malate ligands. The two carboxyl groups and the hydroxyl groups in malate ligand are most probably involved in the formation of the complex, since the formation of a stable complex with the carboxyl groups only is not possible. The malate ligand would therefore occupy three co-ordination positions. One or three molecules of water would be present in the co-ordination in four or six co-ordination complex respectively. Four and six co-ordination complexes of a divalent metal ion (M^{2+}) with malate chelate may be represented by structures (A) and (B) respectively.

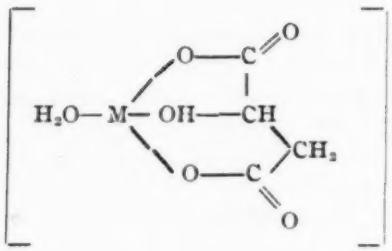


(A)

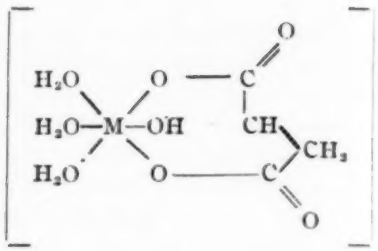


(B)

The water molecules in the above aquo-complexes would ionise to proton and the correspondinig hydroxo-complexes at higher p_H. If the hydroxyl group of malate ligand would form a co-ordinate link with the metal ion without the liberation of a proton, the complex would have been (A_1) and (B_1) respectively without any charge.



(A_1)



(B_1)

These complexes would also ionise to proton and the corresponding hydroxo-complex at higher p_H. It is very probable that when the ligand would be attached to the metal ion, it would occupy three co-ordination positions. The formation of the complex (A) or (B) and (A_1) or (B_1) from the metal ion and the malic acid would result in simultaneous liberation of three and two protons respectively. If the complex formed is 1 : 1 type, it is possible to distinguish between complex (A) or (B) and (A_1) or (B_1) provided that n, the number of proton liberated per metallic ion in the solution, is accurately determined. Besides, the study of the variation of n with p_H would give further information about the 'hydroxo ion.'

The p_H-titration method applied in the study of citrate complexes of nickel and cadmium (Pattnaik and Pani, this *Journal*, 1957, **34**, 673) would be equally suitable for the study of the malate complexes.

Experimental

The chemicals used were Analar quality reagents. A solution (100 c.c.) of malic acid (0.01875 g. mol.) and potassium nitrate (0.25 g. mol.) was titrated against 0.1*N*-NaOH solution and p_H was measured after each addition by a Marconi p_H-meter. The results are graphically shown by curve (A) in Fig. 1. The results obtained in another experiment with exactly the same conditions as above except that 0.0125 g. mol. of copper sulphate was present, is shown in curve (B) in Fig. 1. The p_H of the system containing copper is always lower than the other system under similar conditions. The temperature in both the experiments was 25°.

Discussion

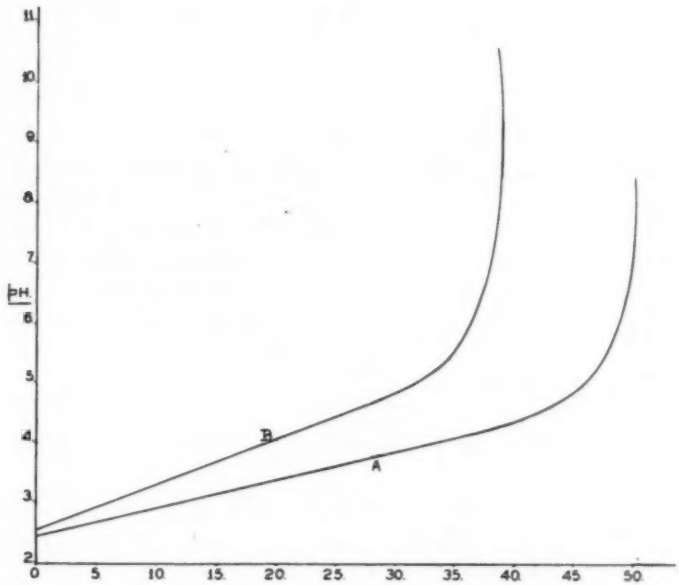
Let A and B be two points on curves (A) and (B) respectively intersected by the p_H axis. The reaction taking place at A due to the addition of sodium hydroxide is

neutralisation of malic acid and the formation of bimalate and malate ions. The reactions taking place at B are neutralisation of malic acid and the formation of the complex. The reaction can be represented by

$$Cu^{2+} + H_2M \rightleftharpoons C + nH^+ \quad \ldots \quad (1)$$

where Cu^{2+}, H_2M, C and H^+ represent the copper ion, malic acid, the complex (charge, if any, is not shown) and hydrogen ion respectively. The equilibrium constant is given by equation (1 : 1) where the square brackets indicate molar concentration per litre.

FIG. 1



NaOH *added (c.c).*

$$\frac{[C] \times [H^+]^n}{[Cu^{2+}] \times [H_2M]} = K \quad \ldots \quad (1:1)$$

Let $[NaOH]_A$, $[M]_A$, $[H_2M]_A$, $[HM^-]_A$ and $[M^{2-}]_A$ be respectively the concentration in g. mol. per litre of sodium hydroxide, total malate, malic acid, bimalate ion and malate ion. The concentrations at B are similarly expressed by $[]_B$. The concentration of total copper at B is equal to that of copper sulphate and is represented by $[CuSO_4]$. The concentration of hydrogen ion is the same at both A and B and is represented by $[H^+]$.

$$[NaOH]_A + [H^+] = [HM^-]_A + 2[M^{2-}]_A \quad \ldots \quad \ldots$$

$$= \frac{k_1}{[H^+]} \cdot [H_2M]_A + 2\frac{k_1 \cdot k_2}{[H^+]^2} \cdot [H_2M]_A$$

where k_1 and k_2 are respectively the first and the second dissociation constant of malic acid ($k_1 = 5.5 \times 10^{-4}$; $k = 2.1 \times 10^{-5}$; Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314).

$$[NaOH]_A + [H^+] = [H_2M]_A \left(\frac{k_1}{[H^+]} + 2 \frac{k_1 \times k_2}{[H^+]^2} \right)$$

or $$[NaOH]_A + [H^+] = a\,[H_2M]_A \quad \ldots \quad \ldots \quad (2)$$

where $$a = \frac{k_1}{[H^+]} + 2 \frac{k_1 \times k_2}{[H^+]^2}.$$

Similarly

$$[NaOH]_B + [H^+] = n[C] + [HM^-]_B + 2[M^{2-}]_B$$

or $$[NaOH]_B + [H^+] = n[C] + a[H_2M]_B. \quad \ldots \quad (3)$$

Subtracting equation (2) from (3) one gets,

$$[NaOH]_B - [NaOH]_A = n[C] + a([H_2M]_B - [H_2M]_A)$$

or $$\Delta[NaOH] = n[C] + a\,\Delta[H_2M] \quad \ldots \quad (4)$$

where $\Delta[NaOH] = [NaOH]_B - [NaOH]_A$ and $\Delta[H_2M] = [H_2M]_B - [H_2M]_A$.

$$[M]_A = [H_2M]_A + [HM^-]_A + [M^{2-}]_A$$

$$= [H_2M]_A + [H_2M]_A \cdot \frac{k_1}{[H^+]} + [H_2M]_A \cdot \frac{k_1 k_2}{[H^+]^2}$$

or $$[M]_A = [H_2M]_A \left(1 + \frac{k_1}{H^+} + \frac{k_1 k_2}{[H^+]^2}\right)$$

or $$[M]_A = b[H_2M]_A \quad \ldots \quad \ldots \quad (5)$$

where $$b = 1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2}.$$

Similarly

$$[M]_B = [C] + [H_2M]_B + [HM^-]_B + [M^{2-}]_B$$

or $$[M]_B = [C] + b[H_2M]_B \quad \ldots \quad (6)$$

Subtracting equation (5) from (6) one gets

$$[M]_B - [M]_A = [C] + b([H_2M]_B - [H_2M]_A)$$

or $$\Delta[M] = [C] + b\,\Delta[H_2M] \quad \ldots \quad (7)$$

where $$\Delta[M] = [M]_B - [M]_A$$

Substituting the value of $\Delta[H_2M]$ from equation (7) in equation (4) one gets

$$\Delta[NaOH] = n[C] + \frac{a}{b}(\Delta[M] - [C])$$

or $$\Delta[NaOH] - \frac{a}{b}\Delta[M] = [C] \times \left(n - \frac{a}{b}\right) \quad \ldots \quad (8)$$

or $$\frac{\Delta[NaOH] - a/b\,\Delta[M]}{[C]} + \frac{a}{b} = n \quad \ldots \quad (9)$$

when the formation of the complex is complete,

$$[C] = [CuSO_4]$$

Hence $$\frac{\Delta[NaOH] - a/b\,\Delta[M]}{[CuSO_4]} - \frac{a}{b} = n \quad \ldots \quad (10)$$

All quantities in the above equation except n can be calculated from the experimental results at different p_H values; the values of n, thus calculated at different p_H values, are recorded in Table I. Below p_H 4, the value of n is less than 2 and above this p_H, n is > 2 and < 3. A complex C, which is formed from copper ion and malic acid is in the process of formation at the lower p_H range. The concentration of this complex increases with increasing p_H and is very nearly complete at about p_H 4. Above p_H 4, the complex C dissociates like a monobasic acid which increases with increasing p_H. The reaction may be represented by

$$C \rightleftharpoons C_1^- + H^+ \qquad (11)$$

$$\frac{[H^+] \times [C_1^-]}{[C]} = K_1 \qquad (11\text{-}1)$$

The equilibrium constant is given by equation (11-1).

Calculation of Equilibrium Constants

Below p_H 4 copper exists in solution partly as Cu^{2+} and partly as complex C. The complex C is formed with the liberation of two protons. Taking n to be 2 and substituting the values of Δ [NaOH], Δ [M] and a/b in equation (9), [C] is calculated at different p_H values (below p_H 4). $[Cu^{2+}]$ is obtained by subtracting [C] from $[CuSO_4]$. $[H_2M]_B$ is obtained from equation (4) or (6). The value of K, thus calculated and shown in the last column of Table I, is fairly constant and the mean value is $3.89 \times .0^{-5}$.

TABLE I

p_H.	ΔNaOH$\times 10^3$.	$-\Delta$[M]$\times 10^3$.	[CuSO$_4$]$\times 10^3$.	n.	[C]$\times 10^3$.	[H$_2$M]$_B \times 10^3$.	$K \times 10^5$.
2.750	2.775	0.520	11.800	0.487	1.649	12.220	4.205
2.875	3.495	0.655	11.470	0.622	2.171	10.590	3.921
3.000	3.990	0.748	11.210	6.747	2.611	9.099	3.336
3.125	4.447	0.834	10.960	0.881	3 089	7.612	2.899
3 250	5.439	1.020	10 690	1.093	4. 62	5.940	3.262
3.375	6.353	1.191	10.420	1.284	5.071	4.457	4.547
3.500	6.676	1.251	10.230	1.456	5.896	3.422	3.975
3.625	7.141	1.339	10.000	1.593	6.676	2.362	4.929
3.750	7.554	1.416	9.781	1.754	7.678		
3.875	7.969	1.494	9.594	1.916	8.833		
4.000	7.884	1.478	9.448	2.015	9.592		
4.125	8.230	1.543	9.260	2.174	11.040		
4.250	8.574	1 607	9.090	2.337	12.840		
4.375	8.504	1.594	8.973	2.440	14.370		
4.500	8.283	1 552	8.865	2.523	16 020		
4 625	8.345	1.564	8.742	2 648	18.770		
4 750	8.191	1.536	8.662	2.732	21.830		
4 875	8.160	1.531	8.590	2.832	26.340		
5.000	7.638	1.432	8.531	2.843	30.120		
5.125	7.300	1.369	8.504	2 867	35.810		
5.250	7.109	1.332	8.474	2.903	43.910		
5.375	6.916	1.296	8.445	2.930	54.640		

Above p_H 4, the concentration of copper ion is very small and, hence, neglected. Copper exists in solution partly as C and partly as C_1^-.

Hence $$[C] + [C_1^-] = [CuSO_4] \quad \ldots \quad (12)$$

For each C and C_1 formed, respectively two and three protons are liberated. Total acid liberated due to the formation of complex is equal $2[C] + 3[C_1^-]$.

Hence $$n = \frac{2[C] + 3[C_1^-]}{[CuSO_4]}$$

or $$\frac{2([C] + [C_1^-])}{[CuSO_4]} + \frac{[C_1^-]}{[CuSO_4]} = n.$$

Since $$[C] + [C_1^-] = [CuSO_4)$$

$$\therefore \quad 2 + \frac{[C_1^-]}{[CuSO_4]} = n$$

or $$[C_1^-]/[CuSO_4] = n - 2 \quad \ldots \quad (13)$$

and $$\frac{[C] + [C_1^-]}{[CuSO_4]} - \frac{[C_1^-]}{[CuSO_4]} = 1 - (n-2)$$

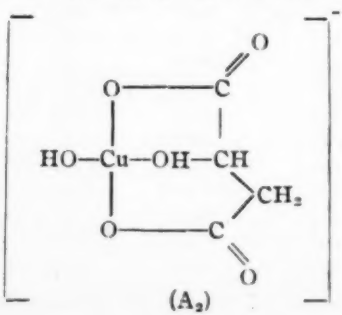
or $$\frac{[C]}{[CuSO_4]} = 3 - n \quad \ldots \quad \ldots \quad \ldots \quad (14)$$

Instead of calculating the exact values of $[C]$ and $[C_1^-]$ for the determination of K_1 by equation (11·1) respectively the values of $[C]/[CuSO_4]$ and $[C_1^-]/[CuSO_4]$ can be substituted. K_1 thus obtained are shown in Table II. It is fairly constant and the mean value is 4.74×10^{-5}.

TABLE II

p_H.	n.	$K_1 \times 10^5$.	p_H.	n.	$K_1 \times 10^5$.
4·375	2·440	3·390	5·000	2·843	5·369
4·500	2·523	3·467	5·125	2·867	4·776
4·625	2·648	4·366	5·250	2·903	5 235
4·750	2·732	4·857	5·375	2·930	5·604
4·875	2·832	6·601			

Structure of the Complex.—The complex C has no charge. It is formed with liberation of two protons. The most probable structure is given by structure (A_1) since copper generally forms four co-ordination. The structure of complex C_1^- is given by either structure A (*vide supra*) or structure (A_2) given below depending on whether the proton is liberated from the hydroxyl group or water molecule in complex C.



(A_2)

DEPARTMENT OF CHEMISTRY
RAVENSHAW COLLEGE, CUTTACK-3.

Received January 2, 1958.

[Jour. Indian Chem. Soc., Vol. 35, No. 5, 1958]

SYNTHESIS OF 8-AMINOQUINOLINES. PART VIII

By A. Raychaudhury, Arun Bose and U. P. Basu

Synthesis of 7-chloro-8-(1′-methyl-4′-diethylaminobutyl)-aminoquinoline has been described.

The substitution of a chlorine atom at the 7-position of 4-dialkylamino-alkylaminoquinolines in place of a 6-methoxy group affords compounds with enhanced antimalarial activity (Andersag, Breitner and Jung, Ger. Patent, 683, 692/1939). In view of the above observation attempts were made to synthesise an analogue of Pamaquin having a 7-chloro substituent in place of the 6-methoxy group. Price and Guthrie (*J. Amer. Chem. Soc.*, 1946, **68**, 1592) attempted to prepare the corresponding compound by the interaction of 7-chloro-8-aminoquinoline with the dialkylamino-alkyl halides. But the reaction did not take place under the conditions tried.

In this laboratory an attempt was made to prepare this type of compounds by the interaction of the sodium derivative of 7-chloro-8-*p*-toluenesulphonamidoquinoline and appropriate aminoalkyl halides and detosylation of the product. Although the intermediate alkylamino-alkyl-*p*-toluenesulphonamidoquinolines were obtained in good yield, the detosylation of the compounds by the various known methods, including that of Weisblat *et al.* (*ibid.*, 1953, **75**, 3630), could not be achieved. Even the use of lithium aluminium hydride for detosylation (cf. Karrer and Asmis, *Helv. Chim. Acta*, 1952, **35**, 1926) proved abortive.

7-Chloro-8-(1′-methyl-4′-diethylaminobutyl)-aminoquinoline was, however, prepared by a different route. 2:3-Dichloronitrobenzene was allowed to react with 1-diethylamino-4-aminopentane to afford 2-chloro-6-nitro-1′-methyl-4′-diethylaminobutylaniline. This was reduced with stannous chloride and the corresponding amine was subjected to the Skraup reaction to yield the desired product. The compound was isolated as the methylene-*bis*-salicylate.

Experimental

7-Chloro-8-p-toluenesulphonamidoquinoline.—A mixture of 7-chloro-8-aminoquinoline (6 g.), *p*-toluenesulphonyl chloride (7 g.) and dry pyridine (10 c.c.) was heated on a water-bath for 3 hours. The mixture was poured into ice-water and the solid filtered, washed with water and dried. After crystallisation from alcohol the solid melted at 152°, yield 5 g. (Found: N, 8.18. $C_{16}H_{13}O_2N_2ClS$ requires N, 8.42%).

Sodium Derivative.—The above compound (8 g.) was suspended in water (30 c.c.) and 10% NaOH solution (10 c.c.) was added. A white pasty mass was formed. Acetone was added to it, filtered, washed with acetone and dried at 100°, yield 8 g.

7-Chloro-8-N-γ-diethylaminopropyl-p-toluenesulphonamidoquinoline.—To the above sodium derivative (8 g.), suspended in dry toluene (100 c.c.), γ-chloropropyldiethylamine (5 g.) was added and the mixture refluxed for 14 hours in an oil-bath. Toluene

was distilled off. The residue was crystallised from ethanol in colorless microcrystalline powder, m.p. 108-10°, yield 5 g. (Found : N, 9.17. $C_{23}H_{28}O_2N_3ClS$ requires N, 9.43%).

7-Chloro-8-N-β-diethylaminoethyl-p-toluenesulphonamidoquinoline was prepared similarly by allowing the sodium derivative of the sulphonamidoquinoline to react with β-diethylaminoethyl chloride, and it was crystallised from ethanol in colorless rectangular plates, m.p. 109-10°. (Found : N, 9.6. $C_{22}H_{26}O_2N_3ClS$ requires N, 9.73%).

2-Chloro-6-nitro-1'-methyl-4'-diethylamino-butylaniline.—A mixture of 2 : 3-dichloronitrobenzene (Kremer and Bendich, *J. Amer. Chem. Soc.*, 1939, **61**, 2658) (10 g.) and 1-diethylamino-4-aminopentane (30 g.) was heated under reflux at 150-60° for 20 hours. The excess of unchanged amine was distilled off at 6 mm. The residue was dissolved in HCl (dil.) and the solution washed with ether. The aqueous solution was basified with NaOH and extracted with ether. The ether extract was dried over anhydrous potassium carbonate. The solvent was then distilled off and the residue distilled under reduced pressure; 10 g. of the required amine was obtained as a reddish yellow oil boiling at 225-30°/6 mm. (Found : N, 13.38. $C_{15}H_{24}O_2N_3Cl$ requires N, 13.40%).

2-Chloro-6-amino-1'-methyl-4'-diethylamino-butylaniline.—To stannous chloride (35 g.) in HCl (conc., 50 c.c.) in a flask, cooled in an ice-bath, the above nitro compound (9 g.), dissolved in HCl (conc., 35 c.c.), was added. The flask was kept sometime in the cooling bath and then gradually heated to 70° when a clear solution was formed. The flask was heated at 80-90° for 2 hours and left overnight at room temperature. Next day, the reaction mixture was dissolved in warm water and poured into excess of iced alkali. The oily product was extracted with ether and the extract dried over anhydrous potassium carbonate. The solvent was distilled off and the residue distilled under reduced pressure to yield 6 g. of a light coloured viscous oil boiling at 208-14°/16 mm. (Found : N, 14.62. $C_{15}H_{26}N_3Cl$ requires N, 14.81%).

7-Chloro-8-(1'-methyl-4'-diethylaminobutyl)-aminoquinoline.—A mixture of the above amine (9 g.), dry glycerine (20 c.c.), arsenic pentoxide (6 g.) and H_2SO_4 (conc.) was cautiously heated at 160-70° for 8 hours. The reaction product was treated with ice and water, and charcoal and filtered. The filtrate was basified with caustic soda, extracted with ether and the ether extract dried over anhydrous potassium carbonate. Ether was distilled off and the residue distilled under reduced pressure, b.p. 180-200°/4-5 mm, yield 1 g.

Methylene-bis-salicylate.—To the above compound (1 g.), dissolved in absolute ethanol, methylene-*bis*-salicylic acid (2 g.), dissolved in ethanol, was added when an oily precipitate was formed. The precipitate was washed repeatedly with dry ether when it solidified The solid was then dried *in vacuo* and finally over P_2O_5 at 100° at 6 mm., m.p. 110-12° (decomp.). (Found : N, 7.4. $C_{18}H_{26}N_3Cl$. $C_{15}H_{12}O_6$ requires N, 6.91%).

BENGAL IMMUNITY RESEARCH INSTITUTE,
CALCUTTA-16.

Received January 2, 1958.

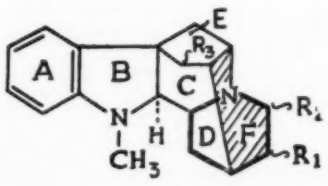
[Jour. Indian Chem. Soc., Vol 35, No. 5, 1958]

STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS. PART I. CONFORMATIONAL ANALYSIS OF AJMALINE, AJMALIDINE, SERPININE AND RAUWOLFININE-THE DIHYDRO-INDOLE ALKALOIDS OF RAUWOLFIA

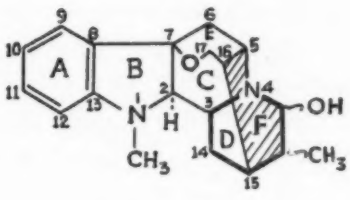
By N. Venkateswaran and Asima Chatterjee

Stereochemical formulation of some of the Rauwolfia alkaloids has been discussed from their conformational analysis.

From *Rauwolfia* genus eight indoline bases, viz., ajmaline, *iso*ajmaline, ajmalidine, serpinine (= tetraphyllicine), rauwolfinine, rauvomitorine, semperflorine (Schlitter and Furlenmeier, *Helv. Chim. Acta*, 1953, **36**, 996) and vomalidine (Hofmann and Frey, *ibid.*, 1957, **40**, 1866), have been isolated. Although much work has been done for elucidation of their structures, very little attention has been paid to clarify their stereochemical formulation. It is therefore intended to take up this study. Ajmaline (Ia) (Chatterjee, Pakrashi and Werner, *Fortshrt Chem. Org. Natur.*, 1956, **13**, 369); Woodward, *Angew. Chem.*, 1956, **68**, 13; Robinson, *ibid.*, 1957, **69**, 40), ajmalidine (Ib) (Djerassi *et al.*, *J. Amer. Chem. Soc.*, 1956, **88**, 1259), serpinine (Ic) and rauwolfinine (II) (Bose, this *Journal*, 1956, **33**, 374; 1958, **35**, 72; Chatterjee *et al.*, *loc. cit.*)-these four indoline alkaloids have been selected for the purpose.



[I]



[II]

a, Ajmaline: $R_1 = C_2H_5$; $R_3 = OH$; $R_2 = OH$.

b. Ajmalidine: $R_1 = C_2H_5$; $R_3 = (> C = O)$; $R_2 = OH$.

c. Serpinine: $R_1 = (= CH.CH_3)$; $R_3 = OH$; $R_2 = H$.

An insight into the configuration of these indoline compounds has been possible from their conformational analysis.

For the construction of the appropriate molecular models of the above bases, the following procedure is necessary:

(1). The piperidine ring C by analogy with *cyclo*hexane (Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44) is to be assigned chair configuration.

(2). The juncture at C/D constituting a reduced pyridocoline system must be considered as *cis* and not *trans*. It has been observed that *trans*-fusion brings C and D approximately in the same plane, separating C_5 (in ring C) and C_{15} (in ring D) wide apart. This arrangement prevents the C_5-C_{15} linkage through a single carbon atom at 16 which is essential for constituting the six-membered ring F (I). But if the juncture is *cis*, rings C and D become non-planar, and a boat configuration for ring D in such a case ensures the desirable proximity of C_5 and C_{15} to construct the ring F.

(3). The alternate chair conformation for ring D has been examined. It creates the same difficulty, *i. e.*, C_5 and C_{15} linkage becomes impossible as they recede far from each other.

Following these conditions, an accurate scale molecular model has been assembled and it reveals the following important stereochemical features of ajmaline, ajmalidine and serpinine molecules:

(*i*). The ring juncture at B/C is *trans*, through the equatorial bonds of C_2 and C_7 (referred with respect to ring C). B and C cannot be *cis*-fused by any means because this arrangement would not permit the construction of the model as would be evidenced in the sequel. *Cis*-fusion of rings B and C would involve linkage through the axial bond of C_2 and equatorial bond of C_7. The pentacyclic ring E involving C_5, C_6, C_7 demands the axial bonds of C_5 and C_7 (*cis* orientation). Hence, the axial bond of C_7 being unavailable for fusion of B and C rings, a *cis*-fusion of these two rings is possible only through the equatorial bond of C_7 and the axial one of C_2. Such a conformation would be unstable as (*a*) they involve heavy substitution on adjacent diaxial bonds and (*b*) the hydrogen at C_2 would be subjected to considerable non-bonded interaction with rings D and E.

(*ii*). The rings C and D are also *cis*-locked through the axial bond of C_3 and equatorial bond of N_4 (with respect to ring C).

(*iii*). C_3-H is equatorial and has α-orientation.

(*iv*). D and F possess boat conformation.

(*v*). D and F constitute a bicyclic ring system with N_4 and C_{15} at the bridgehead positions.

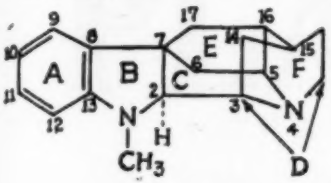
(6). C_3-H and C_{15}-H are *cis*, these orientations being considered in relation to ring D.

It needs mention in this connection that the conformation of serpinine, which bears an exocyclic ethylidene group at C_{20}, does not differ from that of ajmaline and ajmalidine, having an ethyl group at the same carbon atom.

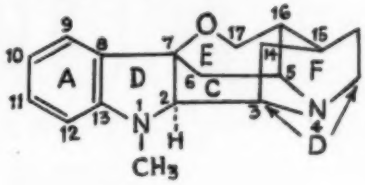
As regards the orientation of -OH at carbon 17, nothing definite can be assessed because the configuration of any five-membered ring is still to be defined.

In rauwolfinine (II), the basic ring skeleton is almost the same as that of ajmaline, ajmalidine and serpinine with the exception that the ring E in (II) is six-membered representing a pyran nucleus. The stereochemical requirements at C_3 and C_{16}

necessitate that this pyran ring should also assume a boat form. C_5 and C_{16} are adjacent carbon atoms of the ring E, and their equatorial and axial bonds are *cis*-oriented. This arrangement results only in a boat and not a chair form for this ring, for adjacent equatorial and axial bonds are *trans* in any chair configuration.



[III]



[IV]

The stereoconfigurations, (III) and (IV), thus established for ajmaline, ajmalidine, serpinine and rauwolfinine, can offer an explanation for (*a*) and (*b*).

(*a*) *The failure of indoline-N-methyl to produce stable salts with acids.*— According to electronic interpretation, indoline -N.CH_3 would be appreciably basic in character and should produce stable salts with mineral acids, which is not the case. The model shows that the rings D and F contribute appreciable steric hindrance towards the approach of the attacking reagent. Should they approach at all, and react with indoline-N.CH_3, the resulting products would be highly strained, unstable and would decompose. This adduces the most logical explanation of the suppressed basic character of indoline-N.CH_3 occurring in dihydroindole alkaloids of *Rauwolfia* genus.

(*b*). *Abnormal carbinolamine reaction (observed in ajmaline).*—Owing to the symmetry of adjacent rings D and F, both being in the boat configuration, the conformationally preferred orientation of any substituent in these rings is difficult to be stated with precision. Any of the substituents, which is in the equatorial coformation with respect to ring D, is as well axially oriented with respect to ring F and *vice-versa*. Substituents in these rings, in whatever conformation they may exist, are considerably hindered owing to (1 : 2H), (1 : 4H) and (1 : 5H) interactions.

Department of Chemistry,
University College of Science and Technology,
Calcutta-9.

Received December 6, 1957.

[redacted]

Tel : 22373 Gram : 'CRUCIBLS'

PLATINUM

LABORATORY APPARATUS

PIONEER MANUFACTURERS IN INDIA

PURE PLATINUM R&Co BOMBAY

TRADE MARK

***WIRES *CRUCIBLES *DISHES *FOILS *TIPPED TONGS *J. LAWRENCE SMITH TYPE CRUCIBLES *SPOONS *SPATULAE *WIRE GAUGE *TRIANGLES**

ALL ITEMS
AVAIABLE FROM READY STOCKS

Reshaping of damaged platinum apparatus undertaken at Rs. 3.25 per gram.
Replacement of damaged platinum apparatus at Rs. 4.25 per gram.

(All prices subject to fluctuation)

Any article in platinum manufactured and supplied as per specification.

CATALOGUE ON REQUEST

All items manufactured from 'Special Platinum' guaranteed 99.9% and over

[redacted]

RAVINDRA & CO. (PLATINUM)
63, DHANJI STREET,
BOMBAY-3.

SPECIALLY MADE

Apparatuses

For

* BOILING POINT TEST

* FREEZING POINT TEST

* ARSENIC TEST

B. P. (1953) Standard.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : East 4411. Gram : Sigamko,

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

INDEX + SIGCOL +

DO YOU KNOW

Sigcol **Index** combines **three** in one ? Behind every **Index** beaker and flask you can see long experience backed by scientific research. **Index** is a symbol of guarantee for laboratory work. It is

* Resistant to Chemical reagents

Resistant to mechanical shocks

* Resistant to heat (coefficient of expansion is only $3.4\ 10^{-6}$).

Sole Distributors :

GHARPURE & CO

P-36, Royal Exchange Place Extn.

Calcutta 1

For Laboratory *Reagent Quality* Acids

To Precise Specifications

Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4:98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3:69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl:35.39% w/w Sp. gr. 1.18 at 15°.
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13

—RELIABLE HOUSE FOR—

* LABORATORY GLASSWARES (Plain and Graduated)
* THERMOMETERS & HYDROMETERS (Various ranges)
* LABORATORY PORCELAINWARES & SILICAWARES
* NICKEL AND PLATINUMWARES
* WHATMAN FILTER PAPERS
* MICROSCOPES & ACCESSORIES
* BALANCES, TINTOMETERS, AEROGEN GAS PLANTS AND OTHER INSTRUMENTS REQUIRED BY CHEMICAL LABORATORIES

Contact :

UNIQUE TRADING CORPN.
221, Sheriff Devji Street
BOMBAY 3

Gram : 'UNILAB Phone : 30011

INDIAN JOURNAL
OF
APPLIED CHEMISTRY

A new bi-monthly publication, published under the auspices of the Indian Chemical Society.

Annual Subscription-Rs. 12/-(Inland)
15/-(Foreign)

Write to the *Hony. Secretary,*

INDIAN CHEMICAL SOCIETY

92, UPPER CIRCULAR ROAD,
P. O. Box No. 10857
CALCUTTA-9

*** FOR YOUR REQUIREMENTS OF ALL KINDS OF EQUIPMENTS FOR RESEARCH ***

RAJ-DER-KAR & CO.,

231, HORNBY ROAD, FORT, BOMBAY-1

Telephone : 26-2304
Telegram : 'TECHLA

A few of our Agencies :

* LUDWIG SEIBOLD, Austria, For p_H Testers, Titrators, and Recorders etc.

EASTMAN KODAK, U. S. A., For All Sorts of Complex Organic Chemicals.

* W.A. TAYLOR & CO., U. S. A., For p_H Comparators, Indicators, Water Analysers etc.

* TRACERLAB Inc., U. S. A., For Radiochemicals & Equipment for Nuclear Research.

Phone – 34-3176. Telegrams—Nadiacheml.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :–

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

NOW ! REMOVE CORROSIVE NEEDLE VALVES FROM ALL YOUR GLASS SYSTEMS WITHOUT RESORTING TO STOPCOCKS

TEFLON* AND GLASS MANOSTAT NEEDLE VALVES **

BURETTES,
SEPARATING FUNNELS,
DISTILLING HEADS,
CHROMATOGRAPHIC TUBES, etc

Made by

THE EMIL GREINER CO., N.Y. U.S.A

Write for Bulletin to

Sole Representatives in India:

LABORATORY FURNISHERS

DHUN MANSION, VINCENT ROAD, DADAR, BOMBAY 14.

Branch: AHMEDABAD. Phone: 6276

* Trade-mark for Du Point Tetrafluoroethylene Resin.
** Patent Applied for.

VERY RELIABLE INDIGENOUS SUBSTITUTES OF GUARANTEED ANALYTICAL REAGENTS MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

BASIC & SYNTHETIC CHEMICALS PRIVATE LIMITED

P O. Jadavpur University, Calcutta-32

GS Gas PLANTS

FOR

HEATING

IN
LABORATORY
INDUSTRY
KITCHEN

GANSONS
PRIVATE LIMITED.

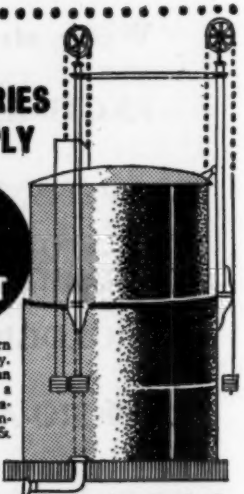
P.O.B. 5576, BOMBAY-14.

——Also makers of——

Superior Laboratory Fittings
Atomic Equipments.

For LABORATORIES GAS SUPPLY

OIL GAS PLANT

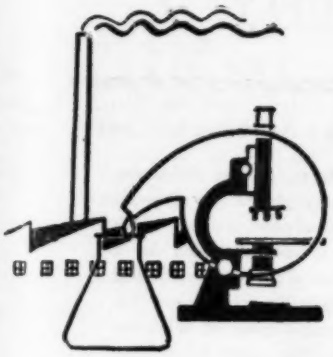


—a must for a modern Laboratory and Industry. We have at our back an experience of many a years in serving Laboratories & Industrial concerns all over India & abroad.

Our Specialities—Fitting of Oil Gas plants, Supply of Science Laboratory Equipments, Furniture & Wood work of all descriptions.

MANSFIELD OIL GAS CO. LD

14, RADHANATH CHOWDHURY ROAD, CALCUTTA 15
Branch—301, LINGHI CHETTY ST., MADRAS 1.



SERVING for LAST 40 YEARS

Laboratory Chemicals & Reagents

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

Acetone
Acid Acetic glacial 99-100%
Alcohol Amyl
Alcohol Methyl
Barium Carbonate
Barium Chloride
Benedicts' Solution
Benzene
Carbon Tetrachloride
Lead Acetate
Liquor Ammon Fort (24/27%)
Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, Panditia Road, Calcutta 29.

BRANCH OFFICES & DEPOTS AT : Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.

PROGRESS IN

CHROMATOGRAPHY 7

PAPER TECHNOLOGY — ITS CONTRIBUTION TO A GROWING SCIENCE

In our previous six advertisements we have described most of the important chromatographic techniques. Throughout, the emphasis has been on the impetus given to organic, inorganic and biochemical analysis by paper chromatography, and on the opportunities for its use that still exist unexploited in many laboratories.

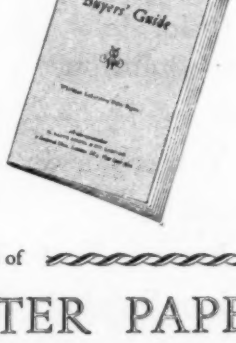
In this, the last advertisement of the series, our concern has shifted from chromatography itself to the paper that makes it possible. A problem the paper technologist has to face is the absence of any complete theoretical account of what happens to solutes and solvents within the cellulose texture. Lacking a definitive physical chemistry, he must apply to paper production not only his technical knowledge, but also an empiricism born of considerable craftsmanship and experience.

It is entirely due to the technologist's skill that papers have been evolved with the diverse properties required by an ever-growing number of chromatographic techniques. By closely controlling the quality of his products, the technologist has produced papers of a purity which compares favourably with that of analytical chemicals.

For many years the Balston laboratories have explored, exploited and advanced the technology of paper at a pace which has entirely satisfied the need for a variety of physical properties embodied in a wide range of shapes and sizes. Today an unexcelled range of Whatman papers can be offered both for chromatography and for its kindred technique, electrophoresis. Papers are made in circle, sheet, strip and the economical reel form. For specialised techniques pattern forms are available or can be cut to order.

Trial packets with a selection of standard papers are marketed for the benefit of laboratories which, as newcomers to chromatography, wish to discover the most suitable paper for their needs.

These and other of the properties and advantages of Whatman filter papers are discussed in the booklet 'Buyers' Guide'. You will find it and its companion Price List useful. Write for free copies to the address below.*



* *It would be of assistance if you would quote the reference CH7 when writing for these booklets.*

H. REEVE ANGEL & CO. LTD
9 BRIDEWELL PLACE LONDON EC4
also at 52 Duane Street New York 7

Sole Distributors of

WHATMAN FILTER PAPERS

(Manufacturers W. & R. Balston Ltd.)

PRESIDENT :

P. K. Bose, D.Sc., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

B. B. Dey, D.Sc., F.R.I.C., F.N.I.
N. R. Dhar, D.Sc., Dr.es.Sc., F.R.I.C., F.N.I.
Sir J. C. Ghosh, Kt., D.Sc., F.N.I.
P. C. Guha, D.Sc., Ph.D., F.N.I.
P. C. Guha, D.Sc., F.N.I.
J. N. Mukherjee, C.B.E., D.Sc., F.A.S.B., F N.I.
Mata Prasad, D.Sc., F.R.I.C., F.N.I.
J. N. Ray, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. Ray, M.A., F.N.I.
B. K. Singh, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

B. Sanjiva Rao, D.Sc., Ph.D., F.N.I.
V. Subrahmanyan, D.Sc., F.R.I.C., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.N.I.
S. Ghosh, D.Sc., F.R.I.C., F.N.I.
President of Allahabad Branch *(ex-officio)*

HONY. SECRETARY :

M. M. Chakrabarty, M.Sc., Ph.D.

HONY. TREASURER :

B. N. Ghosh, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

N. Adhikari, M.Sc.
D. K. Banerjee, D Sc.
D. Chakravarti, D.Sc., F.N.I.
Mrs. Ashima Chatterjee, D.Sc.
B. Chatterjee, D.Sc.
A. C. Chatterji, D.Sc., Dr. Ing., F.N.I.
H. N. Das Gupta, D.Sc.
S. S. Joshi, D.Sc., F.N.I.
T. N. Ghosh, D.Sc., F.N.I.
J. Gupta, D.Sc.
A N. Kappanna, D.Sc , F.N.I.
T. N. Mehta, M.Sc, Ph.D.
R. P. Mitra, D.Sc., F.N.I.
S. M. Mukherji, D.Sc., Ph.D.
S. N. Mukherjee, D.Sc.
P. V. Nair, M.Sc., D.Phil.
A. B. Sen, M Sc., Ph.D.
B. S. Srikantan, D.Sc.
L. M. Yeddanapalli, M.A., Ph.D., D.Sc., F.R.I.C.
S. H. Zaheer, M.A., Ph.D.

HONY. EDITORS :

D. K. Banerjee, D.Sc.
A. N. Kappanna, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

U. P. Basu, D.Sc., F.N.I.
Mrs. A. Chatterjee, D.Sc.
B. Chatterjee, D.Sc.
P. C. Dutta, D.Sc.
B. N. Ghosh, D.Sc., F.N.I.
J. C. Ghosh, D.Sc., F.N.I.
B. C. Guha, D.Sc., Ph.D., F.N.I.
S. S. Joshi, D.Sc., F.N.I.
S. M. Mukherji, D.Sc.
S. N. Mukherjee, D.Sc.
P. Ray, M.A., F.N.I.
S. P. Raychaudhury, D Sc., Ph.D.
P. B. Sarkar, Dr.es. Sc., F.N.I.
S. H. Zaheer, M.A., Ph.D., F.N.I.

HONY. AUDITORS :

P. C. Nandi, M.A., B.Sc., A.C.A.R.A.
A. B. Gupta, B.Sc., L.L.B., A.C.A.R.A.

Asst. Secretary:
K. L. Mukherjee, M.Sc.

Asst Editor :
G. Banerjee, M.Sc.

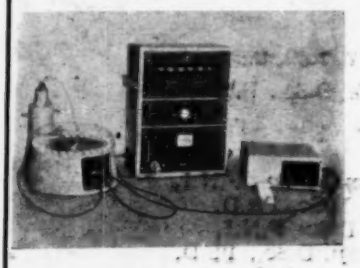
Regtd. No. C1878

FRIESEKE & HOEPFNER

(GERMANY)

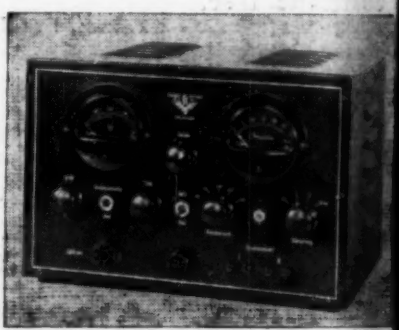
RADIATION MEASURING AND DETECTING INSTRUMENTS & ACCESSORIES *FOR* MEDICAL, LABORATORY & INDUSTRIAL APPLICATIONS

A complete range of instruments for the measurement of X and Nuclear Radiati n, which have always satisfied the exacting demands of industrial and scientific applications, are now available.



The picture shows combined Scaler and Ratemeter FH49 with Automatic sample changer FH448 and Printing Timer FH449.

FH 45 GEIGER MULLER SCALER



Full specifications are available for these and Automatic Chromatogram, Scanner, Measuring Bridge for Radio activity, Electrometer, Scintillation counter, Standard source of Radiation, etc. From

SOLE AGENTS IN INDIA :

TOSHNIWAL BROTHERS PRIVATE LTD.

198, Jamshedji Tata Road, Bombay-1

Branches :

14-B/4, N.E.A. NEW DELHI-5. | 9, Blacker's Road, MADRAS-2. | 172, Dharamtalla St. CALCUTTA-13

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunge, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.